Recent Advances in Tobacco Science

Volume 19

Highlights of Current Research on Tobacco and Tobacco Chemistry

Proceedings of a Symposium Presented at the 47th Meeting
of the Tobacco Chemists' Research Conference

October 18-21, 1993

River Terrace Resort & Convention Center
and
The Edgewater Hotel
Gatlinburg, Tennessee USA

Symposium of the 47th Tobacco Chemists' Research Conference

MENTHOL AND THE DESIGN OF MENTHOLATED CIGARETTES

Symposium Chairman

Thomas A. Perfetti

Program Editorial Committee

S. Wayne McCarty, Chairman
Michael W. Ogden
Harold R. Burton

47th Tobacco Chemists' Research Conference

Contents

Menthol and the Design of Mentholated Cigarettes

Contributors

F. W. Best

M. F. Borgerding

A. J. Borschke

R. Hopp

T. A. Perfetti

J. R. Reid

S. A. Wilson

Preface

Volume 19 of *Recent Advances in Tobacco Science* presents a review of a very important subject to the tobacco industry under the title "Menthol and the Design of Mentholated Cigarettes." The six symposium speakers bring together a wealth of experience and research on the subject, covering topics ranging from the chemistry of menthol to its use in designing mentholated cigarettes.

The Program Editorial Committee thanks each of the authors for their contributions to the symposium program and to this present *Recent Advances in Tobacco Science* edition. Special recognition goes to Thomas A. Perfetti, Symposium Chairman, for his efforts in organizing and coordinating the symposium papers.

S. Wayne McCarty, Chairman
Program Editorial Committee
47th Tobacco Chemists' Research Conference

INTRODUCTION TO SYMPOSIUM

Thomas A. Perfetti

R. J. Reynolds Tobacco Company
Bowman Gray Technical Center
P. O. Box 1487
Winston-Salem, NC 27102

"The most important tool you have is your mind. The most important technique we can ever apply is to keep our minds open." Someone of great insight left us with this deep thought. As we begin this symposium, let us keep our minds open to take in new ideas and concepts to share, nurture, and build on.

This symposium will center on two topics, that to my knowledge, have not been previously reviewed at this conference, namely menthol and mentholated cigarettes. Menthol is one of the primary flavorants employed in the tobacco industry. Mentholated cigarettes represent a major product line, accounting for about 25% of the market in the United States. There is a very large body of works on both topics which will be reviewed today by known experts in their respective fields. It is our hope this symposium will be of great benefit to the industry and to you, the participants. It is also our hope that each of you will find value in this work and that you will be able to apply some of the ideas and concepts to your own situation.

Dr. Rudolph Hopp of Haarmann & Reimer GmbH will discuss the origin of menthol, its chemistry, and its physiological and toxicological properties. Mr. August J. Borschke of R. J. Reynolds Tobacco Company will review technologies relating to menthol use in cigarettes. Mr. Borschke is an attorney and will trace the historical developments of mentholated cigarettes from the patent perspective. Dr. Jack R. Reid of Lorillard Tobacco Company will present a talk concerning the colorful history surrounding the development of the mentholated cigarette market. Dr. Michael F. Borgerding of R. J. Reynolds Tobacco Company will deliver an overview of the chemical determinations of menthol employed in the tobacco industry from an historical perspective. Dr. Steven A. Wilson of Eastman Chemical Company will discuss the theoretical aspects of menthol migration and transfer. Finally, Mr. Fred W. Best of R. J. Reynolds Tobacco Company makes a presentation dealing with effects of cigarette construction parameters on menthol migration and transfer.

Before turning the program over to our first speaker, let me note that we are all indebted not only to our speakers but also to their sponsors who have supported their participation. Additionally, we are also beholden to a host of individuals, groups and institutions, companies and corporations whose investigations and reports and support of research in this field make this symposium possible.

MENTHOL: ITS ORIGINS, CHEMISTRY, PHYSIOLOGY AND TOXICOLOGICAL PROPERTIES

Rudolf Hopp

Haarmann & Reimer GmbH
Corporate Research
Rumohrtalstrasse 1
D-37603 Holzminden, Germany

ABSTRACT

(-)-Menthol, the main constituent of peppermint oils, is the world's second largest aroma chemical. It is shown that the major types of peppermint oil are different with respect to flavor profile and chemical composition. In the biosynthesis of the main constituents, geranyl pyrophosphate is first cyclized enantioselectively to (-)-limonene and then transformed to the oxygenated *p*-menthanes. The stereochemistry of menthol is a good example of structure-odor relationship. Preparation and sensory impressions of the eight enantiomers are described. Cornmint oil (*mentha arvensis*) is still the main source of (-)-menthol, though a few synthetic processes have to be mentioned which have achieved commercial importance. The major sensory property of (-)-menthol is its cooling sensation on the skin or in the mouth. This effect results from a stimulating action on peripheral cold receptors. Some menthol analogues, possessing a longer lasting cooling effect, have been developed and marketed more recently. The reviewed toxicological and biological studies on menthol show that it is nontoxic at levels used in commercial products, not carcinogenic and easily biodegradable.

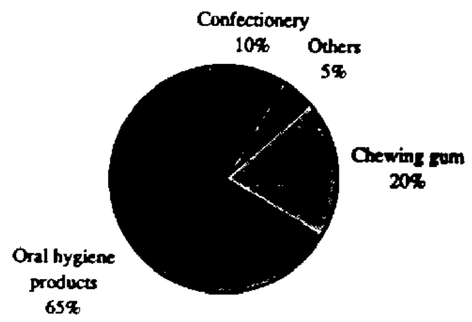
INTRODUCTION

Mint As A Taste Trend

Mint (both peppermint and spearmint) is the world's third most popular flavor complex, being surpassed only by vanilla and citrus flavors. The main applications (Figure 1) consist of oral hygiene products, chewing gum and confectionery. World consumption in 1989 was estimated at more than 10,000 tons (30).

The desire for mint flavors, especially peppermint, was originally an English phenomenon. The *mentha piperita* plant was first cultivated in Mitcham, a town southeast of London (10, 11). From Mitcham, use of this oil as a flavorant spread throughout all English-speaking overseas countries, e.g., Australia, South Africa and the United States. In recent decades, mint flavors have gained increasing popularity on the European continent and in numerous other countries throughout the world. The high acceptance of mint is based not only on its pleasant taste, but also on its association with freshness and cleanliness. An important feature of mint flavor is its cooling sensation in the oral cavity, imparted by (-)-menthol, the main constituent of peppermint oil.

FIG. 1
Main Applications Of Mint Flavors



Peppermint Oils And (-)-Menthol

Besides spearmint oil (from *mentha cardiaca* or *mentha spicata*) which is not reviewed here, peppermint oils and (-)-menthol are the main mint commodities. We have to distinguish between (a) "true" peppermint oil (also known as Mitcham oil, American peppermint oil or *M. piperita* oil) obtained from *mentha piperita* varieties, and (b) cornmint oil (Japanese mint oil, *M. arvensis* oil) obtained from *mentha arvensis* varieties.

The production of *M. piperita* oil is dominated by the United States and amounted there to approximately 3,000 tons in 1992, i.e., more than 90% of the world production. For economic and quality reasons *M. piperita* oil is used almost exclusively as a flavorant.

As a result of its high menthol content of approximately 80%, crude *M. arvensis* oil is always used as a raw material for the production of (-)-menthol. The relatively simple freezing process provides menthol crystals and the remaining oil is known as "dementholated peppermint oil." For years, Brazil (and some parts of Paraguay) was the main growing area with a peak production of around 6,000 tons of crude oil in 1972/1973. Today, China and India contribute 6,000 and 5,000 tons, respectively, to an estimated overall world production of 12,000 tons (Table I).

TABLE I

Suppliers Of (-)-Menthol

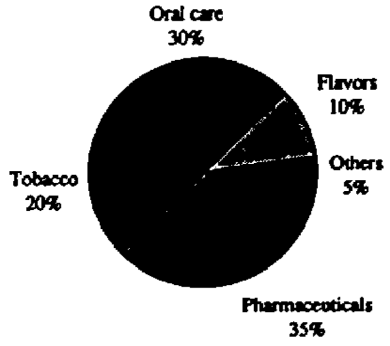
Supplier	1992 Tons[1]	1978 Tons
China[2]	2,300	500
India[2]	750	100
Brazil/Paraguay	350	900
Haarmann & Reimer[3]	1,600	600
Takasago[3]	650	500
Others	650	900
Total	6,300	3,500

[1] Estimated by Haarmann & Reimer Aroma Chemical Division
[2] Not including internal consumption
[3] Synthetic menthol

Though cornmint oil is still the main source of (-)-menthol, many synthetic processes have been developed, starting from natural optically active raw materials, e.g., (+)-citronellal or (+)-3-carene, or from basic organic chemicals, such as m-cresol or isoprene. Only a few processes have been commercially successful. In the past, synthetic menthol was only produced on a smaller scale when menthol prices were high due to shortfalls in the production of natural menthol. These fluctuations in (-)-menthol prices did not end until a few manufacturers (Glidden, Haarmann & Reimer and Takasago) made considerable investments to produce on a large scale (-)-menthol by totally synthetic or semisynthetic means. Today, production of synthetic (-)-menthol accounts for approximately 35% of the world market.

(-)-Menthol is widely used in pharmaceutical, oral care, tobacco, confectionery and perfumed products because of its unique cooling and stimulant effect (Figure 2 and Table II).

FIG. 2
Major Uses Of Menthol



Remarkably, none of the other seven enantiomers of *p*-menthan-3-ol gives rise to a comparable cooling sensation. As will be shown later on, for special uses several cooling agents have been developed, which are less volatile and possess a longer lasting cooling effect compared to (-)-menthol.

TABLE II

Suggested Dosage Of (-)-Menthol In Various Products,
Usually In Addition To Essential Oils
(e.g., Peppermint Oil), Flavors Or Perfumes

Products	Dosage (%)
Pharmaceuticals	
Drugs	0.1
Medicated Oils	2.0 - 4.0
Liniments	2.0 - 3.0
Oral Care	
Toothpaste	0.5
Mouthwashes (Concentrated)	1.0 - 2.0
Tobacco Goods	
Regular Cigarettes	0.003
Menthol Cigarettes	0.1 - 0.2 (Weak Effect)
Menthol Cigarettes	0.25 - 0.45 (Strong Effect)
Pipe Tobacco	0.3
Chewing Tobacco	0.05 - 0.1
Confectionary	
Chewing Gum	0.5
Cough Drops/Lozenges	0.1
Licorice	0.05 - 0.1
Perfumed Products	
Preshave Lotions	0.2 - 0.3
Handkerchiefs	0.1 - 0.2
Foot Sprays	0.5
Refreshing Towels	1.0
Cooling Gels	1.0

Last but not least, (-)-menthol is used in synthetic substitutes of *M. piperita* oil along with some menthol derivatives and other constituents of peppermint oil.

THE ORIGINS OF PEPPERMINT AND MENTHOL

This part is based chiefly upon the review of Landing (19) on peppermint oil and the standard works of Gildemeister and Hoffmann (10) or Guenther (11) on essential oils.

Peppermint and Japanese mint are members of a complex botanical family referred to as *Labiatae* (two-lipped flowers) which is represented in essential oil production (besides mints) by such well-known and widely used plants as rosemary, lavender, basil, sage, and thyme. The genus *mentha*, which includes the true mints, is believed to have originated in the Mediterranean basin and spread from there to the rest of the world by both natural and artificial means.

The major properties of the mints, a delightful aroma and a mildly stinging fresh taste, have been recognized since ancient days. Mints are mentioned twice in the New Testament (Matthew 23:23 and Luke 11:42) and the distillation of mint oil appeared in the literature as early as 410 A.D. in an account written by Synesius of Alexandria, the Bishop of Ptolemais. In the 10th century A.D., a Japanese medical book described the utilization of mint in an eyewash preparation.

In medieval Europe, mints and other useful herbs were cultivated in the monastery and convent gardens. The monks and the nuns compounded from these herbs numerous medicines for the ailments of the day. But it is doubtful if the plant which we know today as peppermint already existed in those times. Specimens of our cultivated *mentha piperita L.*, which is considered a triple cross between *M. sylvestris L.*, *M. rotundifolia L.* and *M. acquatica L.*, were discovered in 1696 near Hertfordshire, England by a Dr. Eales and later in Essex by a Mr. Dale. They were described by John Ray (28). By 1750 peppermint was being commercially cultivated near Mitcham in the county of Surrey, England. Commercial peppermint production moved outward from England to the Netherlands about 1770 and soon spread into Germany, France and the United States. Today, most of the world's production is derived from the so-called English or black mint (*M. piperita* variety *vulgaris L.*). Menthol obtained from peppermint oil was first described by Gaubius in 1771 as "Camphora Europaea Menthae Piperitidis."

Menthol from *M. arvensis* oil has been used in Japan for about 300 years. About 350 A.D., Enzan (a Japanese priest) brought mint plants from China to Japan and planted them in the vicinity of Kyoto, but distillation of Japanese mint and preparation of menthol from mint oil probably did not start before the end of the 17th century (17). Japan advanced to the world's dominant supplier of menthol when, starting about 1870, large acreages of mint were planted on the main island and on Hokkaido. The dominant variety grown in Japan was *M. arvensis* variety *piperascens* Malinvaud. Prior to World War II (1935 to 1939) Japan's annual export of menthol amounted to approximately 300 tons, about 70% of the world market. The balance was furnished mainly by China where primarily *M. arvensis* variety *glabrata* Holmes was grown.

The sudden disruption of supply, due to Japan's entry into the war, encouraged Brazilian entrepreneurs to start with the production of cornmint oil and menthol. *M. arvensis* variety *piperascens* was introduced to Brazil by Japanese immigrants and was first planted in the state of São Paulo about 1936 on a small scale. But later on, virgin land and forest were cleared for this new crop, and menthol production increased rapidly, from a few tons in 1941 to 500 tons in 1945. After the war, production was continued at a lower level and increased again since 1955, reaching a peak of around 3,000 tons in 1973. Since then production has fallen rapidly to around 350 tons in 1992. There have been several reasons for this decrease: (a) limited availability of virgin land suitable for mint cultivation, (b) decreasing attractiveness of mint compared with other crops, (c) competition of China and, more recently, India, and (d) competition of synthetic menthol.

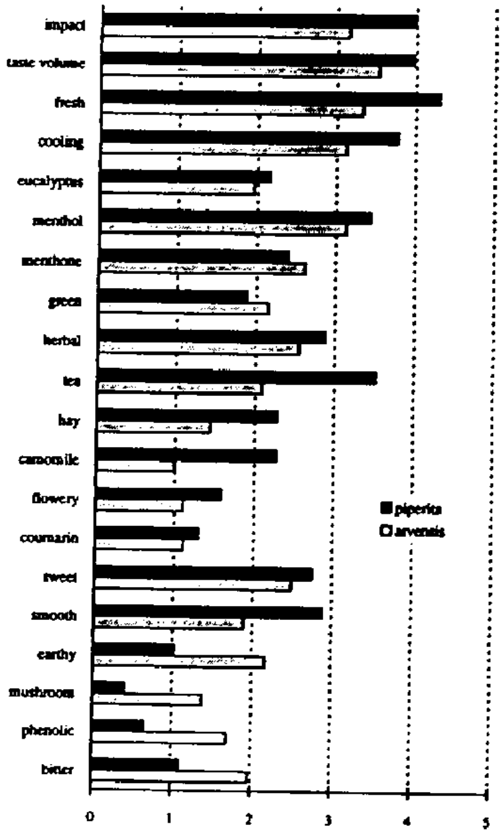
MENTHA ARVENSIS VERSUS *MENTHA PIPERITA* OILS

Flavor Profile

Compared with *M. arvensis*, *M. piperita* oils are significantly more valuable and higher in quality. Their flavor is fresher, richer, sweeter, and more well rounded. As shown in the comparative flavor profiles (Figure 3) such positive flavor characteristics as impact, taste volume (fullness), freshness, cooling, sweetness, and the notes of tea, hay, camomile and flowers are more pronounced in *M. piperita* oils.

FIG. 3

Flavor Profiles Of ***Mentha Piperita*** and ***Mentha Arvensis*** Oil



The harsher flavor of *M. arvensis* oils is characterized by pronounced earthy, mushroomy, phenolic and bitter notes. Some of these differencies can be corrected by rectification; however, the correction is very limited. Therefore, the rectified cornmint oils are merely used as extenders for peppermint oils (30).

Chemical Composition

The chemical compositions of peppermint and dementholized cornmint oil have been the subject of numerous studies (20). As can be seen in Table III, both oils contain similar quantities of the main constituents menthol, menthone, menthyl acetate and neomenthol.

TABLE III

Typical Chemical Compositions Of Peppermint And Dementholized Cornmint Oil: Oxygenated *p*-Menthanes

Compound	Peppermint Oil (%)	Cornmint Oil (Brazil) %
Menthol	40	30
Isomenthol	0.3	Trace
Neomenthol	3	3
Neoisomenthol	0.8	0.4
Menthyl Acetate	4	4
Isomenthyl Acetate	0.3	0.2
Neomenthyl Acetate	0.2	0.05
Neoisomenthyl Acetate	Trace	Trace
Isopulegol	Trace	0.4
Neoisopulegol	Trace	0.6
Isoisopulegol	-	0.5
Trans-Sabinene Hydrate	0.8	Trace
1,8-Cineole	5	0.5
Menthone	22	30
Isomenthone	3	10
Pulegone	1	1
Piperitone	0.5	2
Menthofuran	1 - 4	Trace - 0.2
Menthofurolactone	0.05	Trace

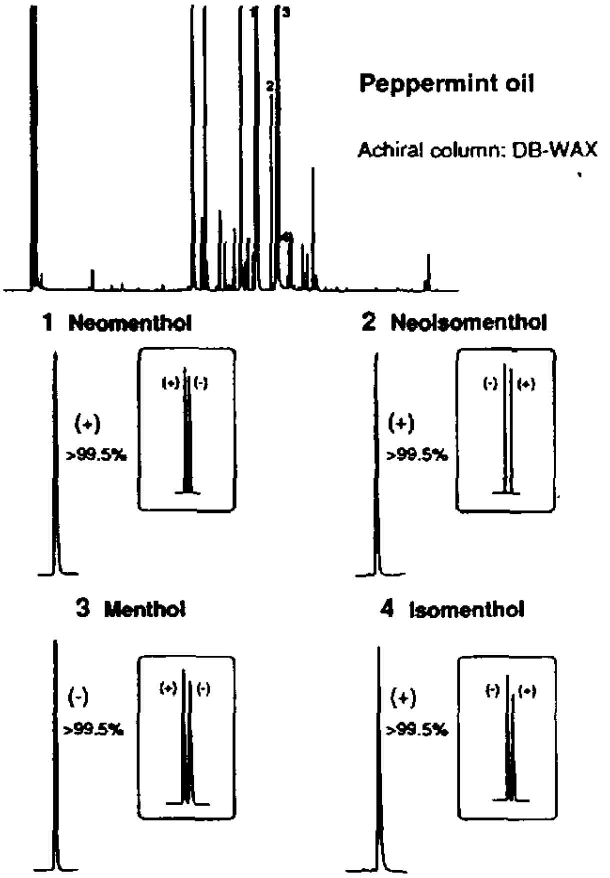
However, valuable flavoring substances, such as 1,8-cineole, menthofuran, sabinene hydrate and menthofurolactone (mintlactone) are found in much higher concentrations in *M. piperita* oil. They are responsible for the positive flavor characteristics of peppermint oil, together with numerous high-impact flavor compounds which have been detected among a total of around one thousand minor and trace constituents. These have been isolated and characterized using high-performance analytical methods and by the systematic evaluation of the organoleptic properties. This was a decisive step toward high-quality synthetic duplicates of peppermint oil (30, 36).

Chirospecific analytical methods have been used to determine the optical purity of various peppermint components (Figure 4, Figure 5 and Figure 6). Werkhoff *et al.* (38, 39) demonstrated that the menthol and menthone isomers in both *M. piperita* and *M. arvensis* oils are almost optically pure (> 99.5%). That is also true for minor components such as menthofurolactone (40). Today, fused silica GC columns coated with modified cyclodextrins are the most powerful tools for the separation of enantiomers. In flavor and essential oil research, usually a preseparation step is necessary. It is possible either by preparative capillary GC (off-line method) or by multidimensional GC (MDGC) including heart-cutting techniques from an achiral preseparation column onto a chiral main-column (on-line coupling).

Biosynthesis Of C3-Oxygenated p-Menthanes

The high optical purity of peppermint constituents is attributed to the stereoselectively controlled biosynthetic steps involved in their formation. Croteau *et al.* have studied the biosynthesis of C3- and C6-oxygenated p-menthanes in *mentha* species for several years and proposed the pathway outlined in Figure 7 (6).

FIG. 4
Optical Purity Of Peppermint Constituents: Menthol Isomers



Chiral column: Heptakis-(2,3,6-tri-O-methyl)-β-cyclodextrin

FIG. 5
Optical Purity Of Peppermint Constituents:
Menthone And Isomenthone

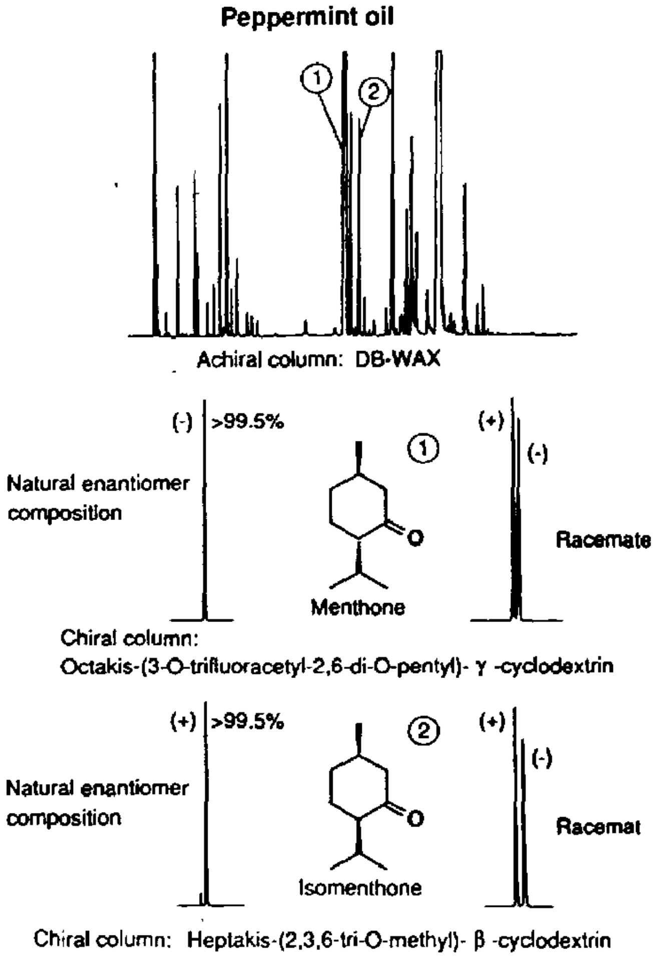
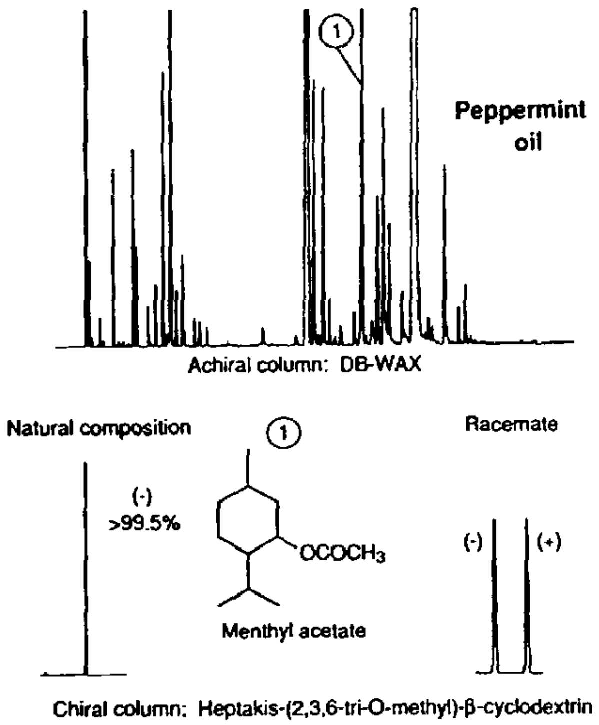
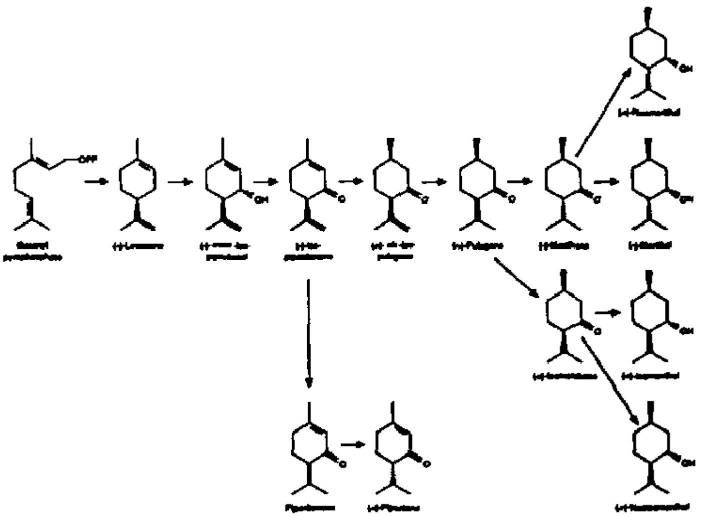


FIG. 6
Optical Purity Of Peppermint Constituents: Menthyl Acetate



The first stage of monoterpene biosynthesis involves a coupled isomerization-cyclization reaction by which the universal C10-isoprenoid precursor geranyl pyrophosphate is transformed to initial cyclic products. In the case of peppermint, (-)-limonene synthase catalyzes the formation of (-)-limonene. The next step, the cytochrome P 450-dependent hydroxylation of (-)-limonene leads specifically to (-)-*trans*-isopiperitenol. An NAD-dependant terpenol dehydrogenase converts (-)-*trans*-isopiperitenol to (-)-isopiperitenone.

FIG. 7
Pathway For The Biosynthesis Of C3-Oxygenated *p*-Menthane Monoterpenes From Geranyl Pyrophosphate



The next step in the sequence is the NADPH-dependent reduction of the $\Delta^{1,2}$-double bond of isopiperitenone to yield (+)-*cis*-isopulegone. The homoallylic double bond of *cis*-isopulegone is then isomerized to the allylic position to afford (+)-pulegone as the product. The enzyme resembles the well-known ketosteroid isomerases in catalyzing an intramolecular hydrogen migration and in requiring no cofactors.

The remaining steps of the sequence are notable for the presence of two stereospecific double bond reductases (NADPH-dependent) for the conversion of (-)-pulegone to (-)-menthone and to (+)-isomenthone, and two stereospecific dehydrogenases responsible for the reduction of (-)-menthone to (-)-menthol and to (+)-neomenthol, respectively. The same two dehydrogenases reduce (+)-isomenthone to (+)-neoisomenthol and to (+)-isomenthol, respectively. The primary metabolites that accumulate in peppermint are (-)-menthone and (-)-menthol.

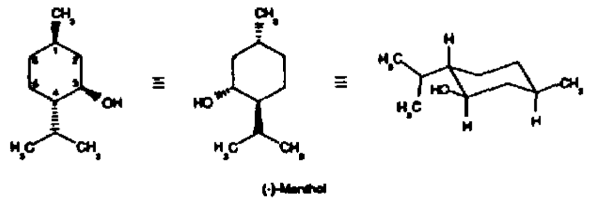
STEREOISOMERS OF MENTHOL

Nomenclature And Graphic Formulas

The work on the structure elucidation and stereoisomerism of menthol, and the preparation of pure stereoisomers, has been shared by many prominent workers, as reviewed by Simonsen and Owen (31) and Merkel.

(-)-Menthol (Figure 8) is one of eight enantiomers of menthol (*p*-menthan-3-ol) owing to three asymmetric centers in the molecule (Figure 9). The *R*,*S* nomenclature and/or space formulas are used to define the absolute configuration, e.g., (1*R*, 3*R*, 4*S*)-menthol for (-)-menthol. In recent years, *Chemical Abstracts* has adopted a combined *R*,*S* and α,β nomenclature (the latter is used in steroid chemistry). Menthol is listed under the name cyclohexanol-5-methyl-2-(1-methylethyl) and the configuration of (-)-menthol is characterized as [1*R*-(1α,2β,5α)].

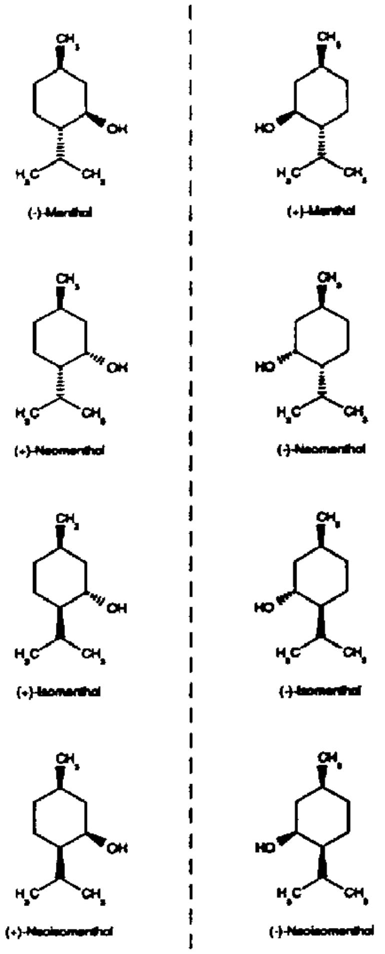
FIG. 8
Various Graphic Formulas Of (-)-Menthol



Preparation And Analytical Data

For sensory evaluations, six of the eight enantiomers of menthol had to be prepared and purified, as both (-) and (+)-menthol were available from the Haarmann & Reimer menthol process. In Table IV, starting materials, methods of preparation and purification procedures are summarized (9).

FIG. 9
The Eight Menthol Stereoisomers



(-)-Menthol (+)-Menthol
(+)-Neomenthol (-)-Neomenthol
(+)-Isomenthol (-)-Isomenthol
(+)-Neoisomenthol (-)-Neoisomenthol

TABLE IV

Preparation And Purification Of Menthol Enantiomers

Prepared Enantiomer	Starting Material, Preparation Method	Separation, Purification
(+)-Isomenthol	Sodium Reduction Of A (-)-Menthone/ (+)-Isomenthone Mixture (77:23)	Rectification, Derivatization (Anisate), Crystallization And Saponification
(-)-Isomenthol	Sodium Reduction Of A (+)-Menthone/ (-)-Isomenthone Mixture (77:23) Which Is Obtained By Oxidation ($Na_2Cr_2O_7$/ H_2SO_4) And Isomerization (NaOH) From (+)-Menthol	
(+)-Neomenthol	$NaBH_4$ Reduction Of (-)-Menthone Provides A 50:50 Mixture Of Menthol And Neomenthol	Rectification, Derivatization, Crystallization (Acetate) And Saponification
(-)-Neomenthol	As Above, Starting From (+)-Menthone Which Is Obtained From (+)-Menthol By Oxidation	
(+)-Neoisomenthol	$NaBH_4$ Reduction Of (+)-Isomenthone Gives 87% Neoisomenthol; (+)-Isomenthone Is Obtained By HPLC Separation	Rectification, Preparative HPLC
(-)-Neoisomenthol	As Above, Starting From (-)-Isomenthone	

Physical and analytical data are listed in Table V.

TABLE V

Physical And Analytical Data Of The Stereoisomers Of Menthol

	Gas Chromatography						
	DB-WAX[1]		DB-1[1]				
Substance	R.I.[2]	Purity	R.I.[2]	Purity	$[\alpha]_D^{20}$	M.P. °C	B.P. °C
(-)-Menthol	1632	100%	1160	100%	-50.2°	} 43	216.5
(+)-Menthol		100%		100%	+50.1°		
(±)-Menthol		100%		100%	-	38	
(-)-Isomenthol	1659	100%	1174	100%	-25.9°	} 82	218.6
(+)-Isomenthol		100%		100%	+24.7°		
(±)-Isomenthol		100%		100%	-	53	
(-)-Neomenthol	1596	99.5%	1148	99.4%	-20.8°	}-15	211.7
(+)-Neomenthol		99.4%		99.5%	+20.9°		
(±)-Neomenthol		99.6%		99.5%	-	52	
(-)-Neoisomenthol	1616	100%	1171	100%	- 2.0°	}- 8	214.6
(+)-Neoisomenthol		99.9%		100%	+ 2.0°		
(±)-Neoisomenthol		98.5%		98.5%	-	14	

[1] Temperature program 60°C - 220°C at 3°C per minute

[2] Retention index

Sensory Characterization Of Menthol Enantiomers (9)

For the reconstitution of peppermint oil, it is important to know the flavor properties of all relevant constituents. Besides others, we compared the (1*R*)-menthols which occur in peppermint oil with the (1*S*)-menthols. All enantiomers were tested in 5% sucrose solution by a test panel of seven experienced flavorists.

In the first step, each substance was evaluated by a dilution profile method to determine the concentration levels of (a) taste threshold, (b) noticeable cooling effect, (c) most acceptable dosage range, and (d) bitter taste. The results are summarized in Table VI.

TABLE VI

Taste Properties Of Menthol Enantiomers: The Dilution Profile (Concentrations: ppm)

	Taste Threshold	Cooling Threshold	Acceptable Dosage	Bitter Threshold
(1*R*)-Menthols				
(-)-Menthol	0.4	0.8	1.5 - 6.0	15
(+)-Isomenthol	0.7	7	1.5 - 4.0	20
(+)-Neomenthol	0.5	2.5	1.0 - 3.0	25
(+)-Neoisomenthol	0.2	> 25	0.5 - 1.5	> 25
(1*S*)-Menthols				
(+)-Menthol	0.3	3	1.0 - 5.0	25
(-)-Isomenthol	0.6	30	1.5 - 5.0	50
(-)-Neomenthol	0.6	25	1.5 - 5.0	30
(-)-Neoisomenthol	1.0	6	2.0 - 5.0	> 25

The taste thresholds of the menthol enantiomers vary within a relatively narrow range of 0.2 to 1.0 ppm. Apart from neoisomenthol, there is only a small difference between the (1*R*) and (1*S*) isomers. However, the cooling level varies significantly and (-)-menthol has by far the lowest cooling threshold. Both (+)- and (-)-neoisomenthol could only be tested up to 25 ppm due to very small amounts of pure substances. The cooling threshold of (-)-neoisomenthol was higher than that concentration. The acceptable dosage range is also quite similar for most of the substances: from about 1 to 5 ppm. The thresholds of bitter tasting were found between 15 ppm and 50 ppm, whereby (-)-menthol surprisingly has the lowest value.

The flavor profiles of (1*R*)-menthols (Figure 10) and (1*S*)-menthols (Figure 11) were determined in a 5% sugar solution at 3 ppm, and each flavor characteristic was scored on a 5 point scale (1 very low; 5 very high). Again, the outstanding flavor properties of (-)-menthol concerning the attributes cool, fresh, minty and sweet were confirmed. (+)-Menthol ranks second with respect to freshness and cooling properties (which is somewhat surprising), but it also has some negative features such as phenolic, musty and bitter. Nevertheless, this result suggests that a <u>pure</u> racemic menthol is not the worst substitute for (-)-menthol. With respect to the constituents of peppermint oil (+)-neomenthol (3%), (+)-isomenthol (0.3%) and (+)-neoisomenthol (0.8%) contribute to the earthy, woody and musty notes. This opens up the possibility for the flavorist to "correct nature" and to develop tailor-made blends with respect to more freshness, sweetness or other desirable characteristics.

FIG. 10
Flavor Profiles Of The (1*R*)-Menthol Isomers

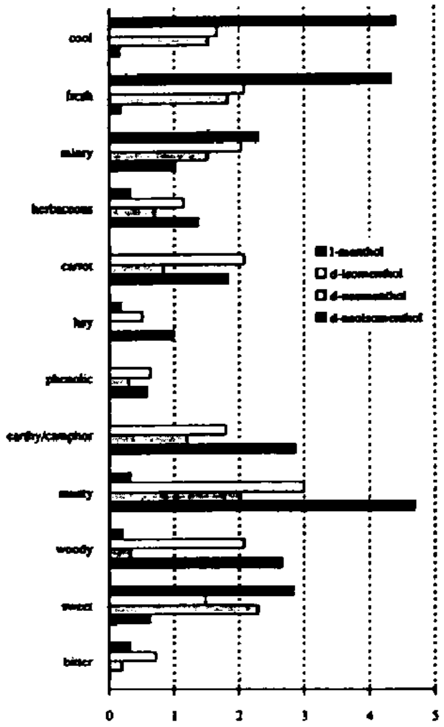


FIG. 11
Flavor Profiles Of the (1S)-Menthol Isomers

SYNTHESIS OF (-)-MENTHOL

Concerning this topic there already exist some excellent reviews (3, 4, 22) which are recommended for in depth studies.

Considerable effort has been devoted to the production of (-)-menthol by synthetic or semisynthetic means from other more readily available raw materials such as (a) dementholized cornmint oil (example *mentha arvensis*), (b) (+)-citronellal (example citronella oil), (c) (+)-3-carene (example Western U.S. and Indian turpentine), (d) (-)-α-phellandrene and

(-)-piperitone (example *eucalyptus dives* oil), (e) (+)-pulegone (example pennyroyal oil), (f) (+)-limonene (example orange oil), (g) racemic menthol (example thymol) via optical resolution, and (h) myrcene (example β-pinene) using an enantioselective isomerization step.

These syntheses, a few of which have been commercially important are shown in Figure 12 to Figure 20 and will be only briefly described here because of the above mentioned reviews. An exception is made with respect to the main processes used today for manufacturing (-)-menthol--the Haarmann & Reimer (Figure 17) and the Takasago (Figure 18 to Figure 20 processes.

"Classical" Menthol Syntheses (Figure 12)

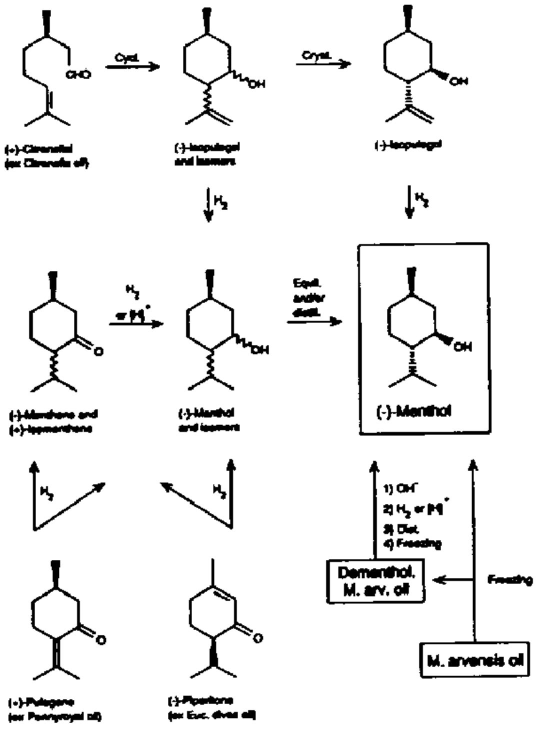
From Dementholized Cornmint Oil: This relatively inexpensive by-product of natural menthol production is still rich in menthol, menthone and some other components which can be transformed to menthol (see Table III). Hydrolysis of menthyl acetate, mild reduction of menthones or hydrogenation respectively, followed by distillation and crystallization, yields additional (-)-menthol.

From (+)-Citronellal (Example *Citronella*): This process has been used widely whenever the supply of natural menthol was short. (+)-Citronellal can be isolated with an optical purity of approximately 80% from citronella oil. Accordingly, it is cyclized by acidic catalysts (e.g. silica gel) to give a mixture of optically active isopulegol isomers and 20% of the corresponding racemates. Preferably, (-)-isopulegol is separated by crystallization at low temperatures and directly hydrogenated to pure (-)-menthol. The alternative procedure of hydrogenating the isopulegol mixture and separating (-)-menthol from its isomers requires derivatization.

From (-)-Piperitone (Example *Eucalyptus Dives*): This process has been used in Australia on a smaller scale. (-)-Piperitone isolated from *eucalyptus dives* oil usually is already partially racemized, due to the unstable asymmetric center at C4, adjacent to the carbonyl group. Moreover, the hydrogenation to either (+)-isomenthone or to an isomeric mixture of menthols is not completely chirospecific with respect to the newly formed chiral center at C1. Therefore, (-)-menthol has to be purified via derivatization.

<u>From (+)-Pulegone (Example Pennyroyal Oil)</u>: Hydrogenation and reduction of the (-)-menthone/(+)-isomenthone mixture with nascent hydrogen gives predominantly (-)-menthol. However, the actual price of pennyroyal oil is prohibitive for commercial production.

FIG. 12
"Classical" (-)-Menthol Syntheses



---

*[H] H in statu nascendi

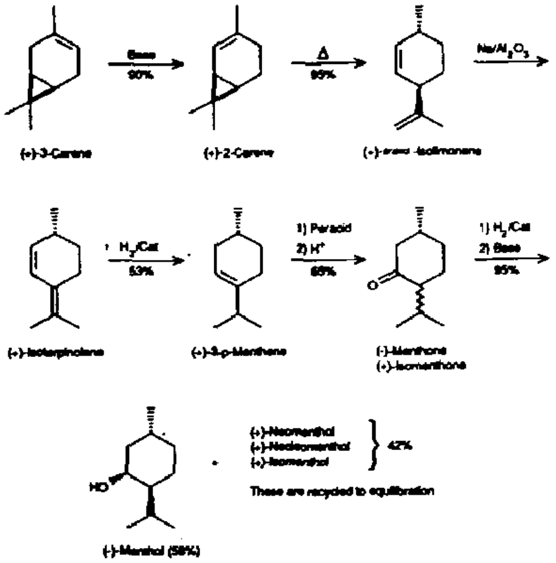
(-)-Menthol From Various Natural Terpenes (Figure 13)

From (+)-3-Carene: The MRC-Process (MRC = Malti-Chem Research Centre, Nandesari, Vadadora, India) starts from (+)-3-carene, the major component of Indian turpentine oil (55% to 65%). Base catalyzed isomerization provides (+)-2-carene which is pyrolyzed to (+)-*trans*-2,8-*p*-menthadiene, followed by an isomerization step to (+)-isoterpinolene in the presence of strong bases. Hydrogenation to (+)-3-*p*-menthane, epoxidation and subsequent rearrangement provide a menthone/isomenthone mixture which is reduced and purified in the usual way (34). A drawback of this process is a partial racemization which has its origin in the isomerization step to isoterpinolene (24). It is obvious that a multistep process like this can only be competitive on a rather large scale. Again, a pure (-)-menthol is only obtained via derivatization.

Alternatively, (+)-*trans*-isolimonene can be hydrochlorinated-dehydrochlorinated to give (+)-isoterpinolene. A second hydrochlorination followed by treatment with sodium acetate and acetic acid yields a mixture of *cis* and *trans*-pulegyl acetate which is hydrolyzed to (-)-*cis*- and (+)-*trans*-pulegol. Because the absolute configuration of C1 is fixed in this pathway, hydrogenation of either pulegol provides (1R)-menthols which can be equilibrated and separated as previously described. This promising route, developed by Hercules, Incorporated, has not been commercialized (Figure 14).

FIG. 13

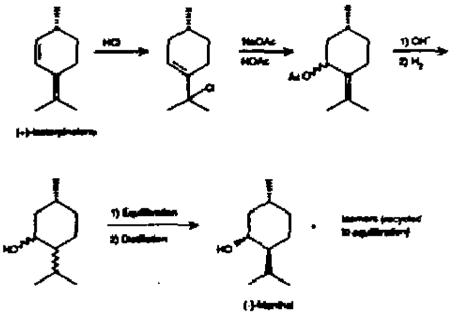
(-)-Menthol From (+)-3-Carene: The MRC-Process (India)*



* MRC = Malti-Chem Research Centre, Nandesari, Vadodara, India

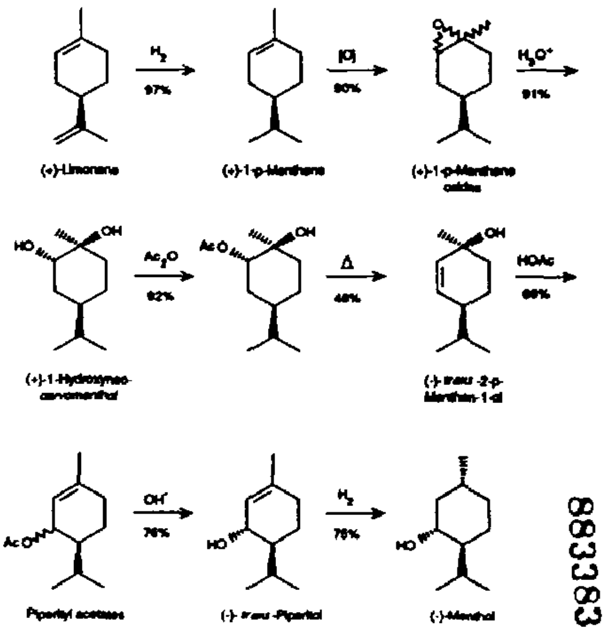
FIG. 14

(-)-Menthol From (+)-3-Carene: The Hercules Route



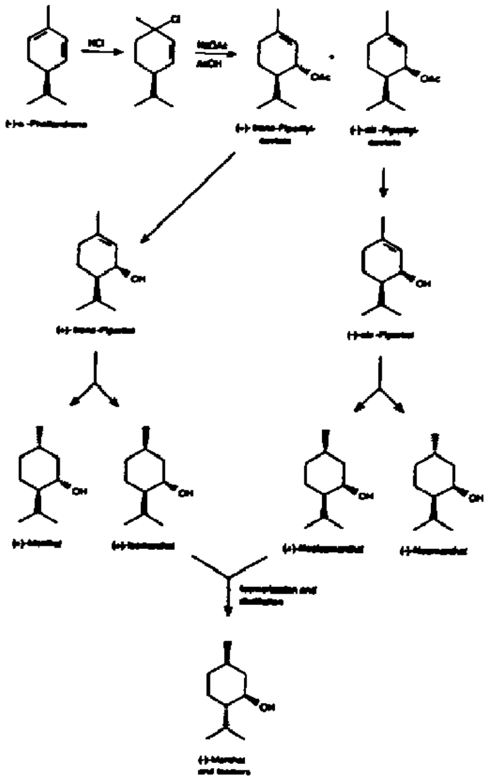
From (+)-Limonene (Figure 15): Optically pure (+)-limonene is an inexpensive by-product from the citrus industry. Hydrogenation to (+)-1-p-menthene and air oxidation in acetaldehyde yields (+)-1-menthene epoxides economically. These are hydrolyzed to (+)-1-hydroxyneocarvo-menthol and acetylated to give the desired (+)-1-hydroxyneocarvomenthyl acetate which is then pyrolyzed to (-)-*trans*-2-*p*-menthen-1-ol. Via piperityl acetate (by acetylation and allylic rearrangement) and (-)-*trans*-piperitol, (-)-menthol is finally obtained by hydrogenation containing 25% (-)-isomenthol. This (1*S*)-isomer cannot be transformed to (-)-menthol. The drawback of this interesting route is its low overall yield.

FIG. 15
(-)-Menthol From (+)-Limonene: The Reynolds Route



From (-)-α-Phellandrene (Figure 16): (+)-Trans-piperitol obtained via piperityl chloride can be hydrogenated to give a mixture of 97% (+)-isomenthol and 3% (+)-menthol. (+)-Isomenthol can be converted to (-)-menthol by crystallization, equilibration and distillation. The process suffers from the disadvantage of by-products and isomer separation.

FIG. 16
(-)-Menthol From (-)-α-Phellandrene: The Glidden Route



The Haarmann & Reimer (-)-Menthol Process (Figure 17)

Around 1965 Haarman & Reimer decided to develop a total synthesis of (-)-menthol starting from thymol. Hydrogenation of thymol produces a mixture of isomers containing all eight menthol enantiomers, although (-)-menthol is the only target product (16).

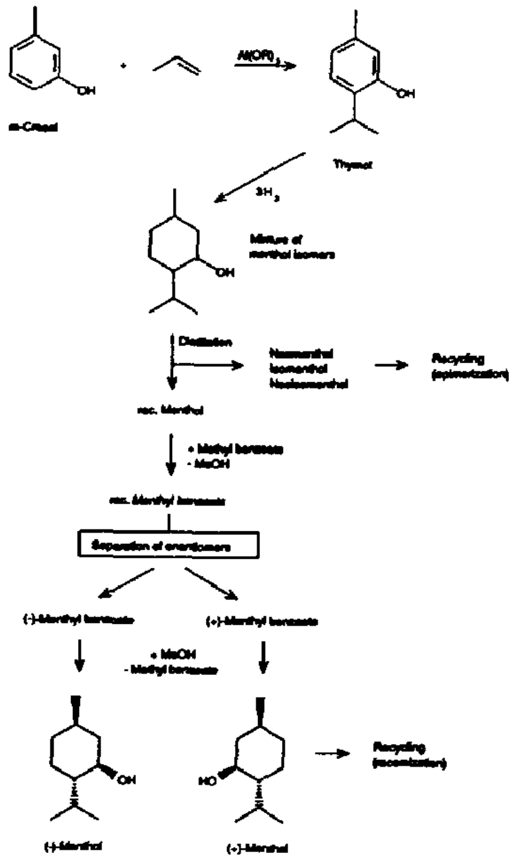
The difficult part of the synthesis is first to separate (±)-menthol from the other isomers and then to separate it into (-)- and (+)-menthol. For economic reasons (+)-menthol and the other remaining menthol isomers have to be recycled.

Figure 17 shows the various stages in the H&R menthol process. o-Alkylation of the m-cresol produces thymol which, on hydrogenation, gives a mixture of approximately 58% to 60% (±)-menthol, 28% neomenthol, 12% isomenthol and 1% neoisomenthol. After distillation, (±)-menthol of approximately 99% purity is obtained which is esterified to menthyl benzoate. The most important step is then to separate the benzoates into the enantiomers (2). Finally, the benzoates are transesterified once again to form (+)- and (-)-menthol and methyl benzoate which is recycled to the production process.

The crucial step of this process, as mentioned above, is the enantioselective crystallization of (-)- and (+)-menthyl benzoate, carried out continuously in two separate vessels, by seeding a supersaturated solution of (±)-menthyl benzoate with crystals of the (+)- and (-)-form respectively. We did of course attempt the enantioselective crystallization of (±)-menthol, but the melting point diagrams showed that (±)-menthol crystallizes as a racemic compound and not as a mixture of (+)- and (-)-menthol crystals. All our efforts to bring about selective crystallization in a variety of solvents were to no avail. On the other hand, crystallization of (±)-menthyl benzoate, while involving an additional stage of purification, does in fact enhance the quality of menthol. The overall yield of the H&R process, based on the starting material thymol, is more than 90%.

The H&R menthol plant in Bushy Park near Charleston, South Carolina, USA went on stream in 1978. The menthol plant in Holzminden has been in operation since 1973.

FIG. 17
Total Synthesis Of (-)-Menthol From m-Cresol:
The Haarmann & Reimer Process

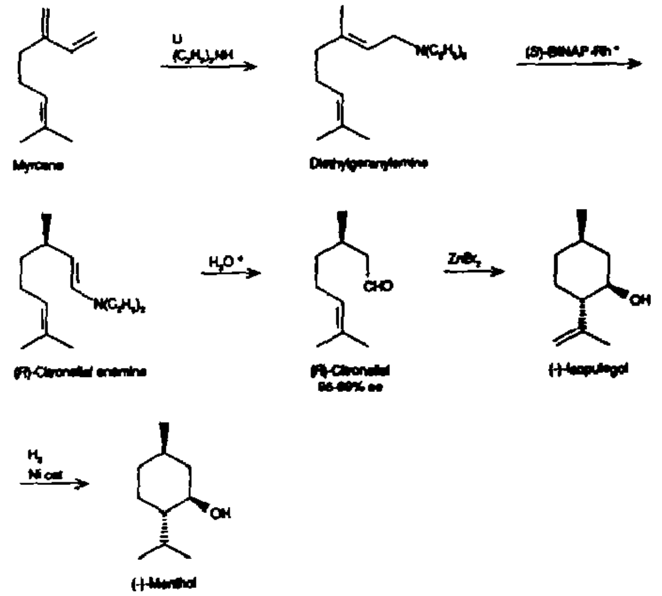


The Takasago Synthesis Of (-)-Menthol From Myrcene (Figure 18)

Biochemical methods for enantioselective hydrolysis of racemic menthyl esters have been developed by Takasago Perfumery Company (13) in the late 1960's, but we have no confirmed information if this method was utilized for the resolution of (±)-menthol (from thymol) into its optical antipodes on a technical scale.

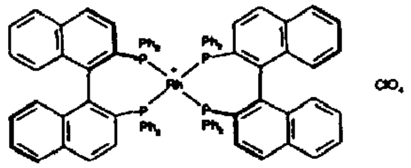
FIG. 18

The Takasago Synthesis Of (-)-Menthol From Myrcene



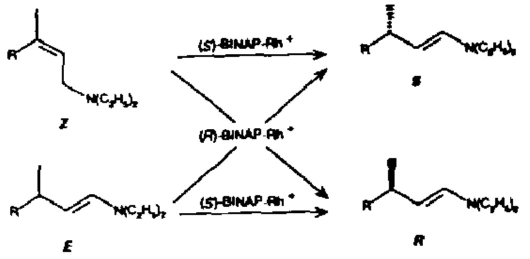
For about ten years, Takasago International Company has been manufacturing (-)-menthol from myrcene (27). First, the triene is converted in a regio- and stereoselective manner to diethylgeranylamine by lithium catalyzed addition of diethylamine. The key step is the subsequent BINAP-Rh(I) catalyzed enantioselective isomerization of the allylic amine in THF giving (R)-citronellal enamine in 96% to 99%. The chiral catalyst used in this step is shown in Figure 19.

FIG. 19
Chiral Rhodium BINAP Complex, The Key
Catalyst In The Takasago Synthesis



Enantiomeric purity of the chiral aldehyde obtained by hydrolysis is much higher than natural citronellal from citronella oil. Stereoselective cyclization of (R)-citronellal promoted by zinc bromide, giving isopulegol, followed by catalytic hydrogenation completes the synthesis of menthol. The technical refinement of the Rh catalyzed asymmetric reaction has enabled the process to work up to a 9-ton scale, where the turnover number (produced enamine mol/Rh catalyst mol in 18 hours) approaches 8,000 per cycle. The BINAP-Rh complex catalyst can be recycled efficiently, giving the overall turnover number of 400,000. This isomerization is chirally flexible leading to either natural or unnatural citronellal enamine. In addition to geranyl- and nerylamines, a variety of allylic amines can be isomerized in an enantioselective and predictable manner. The general scheme is given in Figure 20 (16).

FIG. 20
Rhodium BINAP Catalyst: Stereochemical
Correlation Between Substrate, Catalyst And Product



PHYSIOLOGICAL EFFECTS OF MENTHOL

The Response Of Various Receptors To Menthol

Early investigators clearly demonstrated that menthol affects the response of many receptors to stimulation. Like many other substances, the response to menthol is enhanced in small concentrations and depressed in large concentrations or after extended exposure. The electrophysiological response to menthol was first demonstrated for thermal receptors (8, 15). Similar responses to menthol were observed in chemoreceptors of the carotid body. Carotid bodies are regions of receptors located in the neck area which are sensitive to substances that stimulate and transmit information to the brain, particularly the medulla and brain stem (18).

An increase as well as a decrease in sensitivity to menthol after sustained menthol exposure has been observed for the olfactory sense (32) and the gustatory (taste) sense (33). These studies employed psychophysical techniques which require scaling measurements of perceptual responses rather than the recording of impulses from the receptor cells themselves.

To bridge the gap between the electrophysiological technique used in the studies of nongustatory receptors and the psychophysical technique used in the studies of gustatory receptors, Hellekant (14) investigated the electrophysiological effects of menthol on gustatory receptors. The excitability of the gustatory receptors was evaluated by recording the impulse activity in the *chorda tympani* nerve of the cat. It was observed that menthol elicited a slowly increasing activity in all gustatory fibers. Adding menthol changed the gustatory response to sapid solutions [concentration of sapid solutions (nonoffensive levels of agreeable flavor solutions) was (aqueous) 0.01 M quinine-monohydrochloride, 0.05 M acetic acid, 0.5 M sodium chloride, 1 M sucrose and 2.5 M ethyl alcohol--menthol solution concentrations were 0.05, 0.1 and 0.2 gram per liter (aqueous)] in two respects: (a) it slightly suppressed the initial burst of activity and (b) it enhanced the sustained response. Rinsing with menthol left the gustatory receptors with a changed sensitivity to stimulation with other sapid solutions. This effect on the receptors was related to concentrations and length of the preceding menthol rinse. It also showed variation with regard to stimulus, concentration, and subject.

Recent studies on the sensory transducer mechanism of nasal and lingual cold receptors have demonstrated that menthol activates cold receptors by interfering with the calcium conductance of the neuronal sensory membranes (29, 35).

The Cooling Effect Of Menthol And Menthol Analogues (37)

Menthol does not cool by volatilization. The cooling effect seems to result from chemical action at or near those nerve endings which are associated with the sensation of cold. When menthol is placed on the lingual nerve of the cat, the cold fibers of that nerve are either provoked into firing or, if already firing, respond with a higher rate of firing. Since the neurophysiological basis of the response to cold is essentially the same in all mammals, including man, and since there are many common features in the action of menthol and synthetic cooling agents, it seems reasonable to assume that all such coolants act by a common mechanism, which is essentially that of a stimulant-receptor interaction. Cooling responses can be produced as a result of nasal, oral, or topical application.

Molecular Requirements For Cooling Activity (37): It has been established that four important criteria must be satisfied for a compound to possess effective cooling activity: (a) a hydrogen bonding group, (b) a compact hydrocarbon skeleton, (c) a correct hydrophilic/hydrophobic balance, and (d) a molecular weight in the range 150 to 350.

Hydrogen Bonding: A hydrogen bonding function is essential for cooling action. We believe that the function must contain an oxygen atom capable of acting as a hydrogen bond acceptor. For greatest cooling activity, strong hydrogen bond accepting capability is necessary. There is no indication that the provision of more than one hydrogen bond accepting group in the molecule enhances the cooling effect; some *p*-menthanediols are active, but none is as active as (-)-menthol.

Hydrocarbon Skeleton: It is assumed that the functional group takes part in hydrogen bonding at a receptor site, and that for cooling, the hydrocarbon portion or portions of the molecule must provide a compact hydrophobic region near to the site of hydrogen bonding.

Hydrophilic/Hydrophobic Balance: For strong cooling activity, a compound must have the correct hydrophilic/hydrophobic balance. This balance is important in stimulant-receptor interactions. The most common measure of hydrophilic/hydrophobic balance is the Hansch log P value, where P is the partition coefficient of the compound between *n*-octanol and water. The log P value is well established as an important factor of the pharmacological activity and it is also recognized as one of the factors which determines the rate of transport of compounds through biological membranes, especially the skin.

The log P values of cooling compounds were calculated from published tables of the substituent values. Strong cooling compounds have log P values in the relatively narrow range of 1.5 to 4.0 and values for nearly all cooling compounds lie in the range of 1.0 to 5.0. The log P value of menthol is 3.1.

Molecular Weight: If a hydrocarbon skeleton capable of giving strong cooling compounds is combined with a strong hydrogen-bond accepting functional group, and if the log P value of the resultant molecule is in the correct range, then cooling will be observed if the molecular weight is in the range 150 to 350. The criterion of molecular weight is more flexible than the criteria for hydrogen bonding, skeleton and log P.

General Properties Of Cooling Compounds: Apart from the cooling effect and a degree of flavor potentiation and odor modification, there are no common sensory properties of cooling compounds. For instance, there is no association between minty smell and cooling.

Because there are many structural variations in cooling compounds, the physical properties of these compounds also vary. Most cooling compounds are solids, although liquids are not uncommon when the functional group is hydroxyl or N,N-dialkylcarboxamide. In addition, most of them are readily soluble in common organic solvents but, due to the requirements of the log P value, all have very limited solubility in water. It should be noted, however, that saturated aqueous solutions have readily perceptible cooling effects. The alcohols and N,N-dialkylcarboxamides are, in general, volatile and some are odorous with odor types ranging from minty to fruity and from earthy to camphoraceous.

Other Sensations Produced By Cooling Compounds

All cooling compounds produce sensations other than pure cooling including tingling, stinging, burning and bitter. These other sensations are most readily described by reference to a strong peppermint candy, which produces tingle in the mouth and, if strong enough, a burning sensation. Compounds differ in the relative degree of cooling and other sensations. Those compounds that produce little sensation other than cooling are (in our terminology) high "quality." The relative degree of cooling appears to correlate to some degree with compound type. For example, hydroxyesters and hydroxyacetals tend to produce low levels of sensations other than cooling.

These sensations are dose sensitive. In general, increasing the dose of the cooling compound beyond a certain limit gives no apparent increase in cooling. However, it does cause an increase in other sensations, finally to the point where the other sensations dominate the cooling effect.

Sensitivity Of Different Parts Of The Body

Parts of the body differ greatly in their sensitivity to cooling compounds. No attempt has been made to determine their relative sensitivities in absolute terms; however, the suggested order of sensitivity is: eye >> tongue > interior buccal region > ano-genital area > lip > trigeminal area > other face areas > axilla > inside forearm, breast > other arm areas, thigh, back, hands, feet >> palms, soles. The eye is extremely sensitive with thresholds probably measurable in nanograms and a simple test for cooling effect in a volatile compound is to hold the opened bottle near the eye. This test with menthol gives a sharp and very obvious sensation which agrees with consumers' comments on the effect of mentholated shaving foam on the eye.

Like menthol, synthetic cooling compounds also give a cooling sensation in the lungs (when added to cigarettes or inhaled as an aerosol spray) and to the gastrointestinal tract (when ingested).

The order of sensitivity clearly follows a general order of increasing thickness of *stratum corneum*. It seems probable that the sensitivity of an area is determined mainly by the ease with which the compound can penetrate this barrier. For example, abraded or hydrated forearm skin has a reduced threshold compared to intact skin. Although the barrier role of the *stratum corneum* is probably dominant, it is also likely that the number of cold-sensitive nerve endings per unit area and the efficiency with which the central nervous system processes nerve signals vary with the location on the skin.

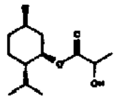
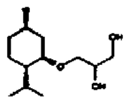
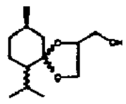
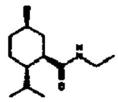
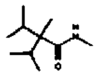
Mechanism Of Action

When a composition containing a cooling compound is applied to various body surfaces, three processes must occur before a cooling effect is perceived: (a) molecules of the compound must transfer from the vehicle and must penetrate the surface of the *stratum corneum*, (b) molecules must diffuse through the skin, and (c) molecules must interact with the receptors.

The role of each of the three processes in producing the cooling effect is dependent upon (a) the properties of the compound, (b) the kind of solvent or formulation in which the compound is used, and (c) the properties of the body surface to which it is applied.

Some commercialized cooling compounds are shown in Figure 21 including one which is in the development stage.

FIG. 21
Various Cooling Compounds

Structure	Trade Name	Origin / Patents
	Frescolat ML Trivent ML	HAARMANN & REIMER TRIVENT, USA
	Cooling Agent No. 10	TAKASAGO PERFUMERY CO. EP 80 148 (1981)
	Frescolat MGA -	HAARMANN & REIMER DOS 41 10 973 (1991) WRIGLEY EPA 465 170 (1991) US Priority 1990
	WS 3	WILKINSON SWORD, GB (STERLING ORGANICS / PRODUCER) US 4 150 052 (1979) UK Priority: 1971
	WS 23	WILKINSON SWORD, GB (STERLING ORGANICS) UK 1 421 744 (1972) UK 1 421 471 (1974)

TOXICOLOGICAL AND BIOLOGICAL PROPERTIES OF MENTHOL

Menthol is one of the most thoroughly studied flavor and fragrance materials with respect to toxicology and biological properties. Many of these data are summarized in a monograph (26) and other reviews (5, 7). The essential results are briefly reported.

Regulatory Status: Menthol has been given generally recognized as safe (GRAS) status and is approved as a direct food additive by the FDA. The Council of Europe (1981) has also approved menthol for food use, giving an acceptable daily intake (ADI) of 2 milligrams per kilogram for total menthol and menthyl esters. In addition, the Joint FAO/WHO Expert Committee on Food Additives (1968) has published a monograph and specifications for menthol listing an unconditional ADI of 0.2 milligram per kilogram.

Acute Toxicity: The oral, sc and ip LD_{50} values are in the range of 0.8 gram per kilogram to 6 grams per kilogram in rats, mice and cats. The inhalation RD_{50} level for menthol has been determined to be 760 mg/m^3 (116 ppm) for Swiss-Webster mice (1). The RD_{50} is that concentration capable of inducing a 50% reduction in mean respiratory frequency.

Short-Term Toxicity: No detrimental effects of menthol were observed in short-term biological studies.

Carcinogenity: Menthol is not carcinogenic, as shown in studies by the National Cancer Institute (25).

Genotoxicity: Litton Bionetics (23) conducted a mutagenicity study on menthol using the host-mediated assay, cytogenetic studies, and the dominant lethal assay. The results of all three assays were negative. Menthol pyrolysate was tested against *salmonella typhimurin* strains (21) with negative results.

Metabolism (26): The urinary metabolite of menthol was identified as menthyl glucuronide in several species.

Some test results on Haarman & Reimer menthol, concerning skin irritation and sensitization are summarized in Table VII.

TABLE VII

Survey Of Safety Studies For H&R Menthol: Irritation And Sensitization Tests

Test	Dose % Vehicle	Species	Test Results
Skin Irritation (OECD 404)[1]	100, 50, 25 25, 5, 1, 0 DEP	Rabbit	Irritation At 100% And 50%
Skin Irritation (Not OECD)[2]	100	Guinea Pig	No Irritation
Skin Sensitization Buehler (OECD 406)[3]	25 EtOH/DEP	Guinea Pig	No Sensitization
Skin Sensitization (Not OECD)[2]	100	Guinea Pig	No Sensitization
Eye Irritation (OECD 405)[1]	28.6 DEP	Rabbit	No Irritation
Eye Irritation (OECD 405)[1]	50 DEP	Rabbit	Slight Irritation
Eye Irritation (Not OECD)[2]	10, 20, 30 40, 50, 60 Olive oil	Rabbit	No Irritation

[1] Author - K. Skydshaard; date - August, 1989
[2] Author - G. Hopf; date - April, 1974
[3] Author - J. Cuthbert; date - February, 1991

A few ecotoxicological data are listed in Table VIII, showing that menthol is readily biodegradable.

TABLE VIII

Ecotoxicological Data For H&R Menthol

Test	Results	Author/Year
Biodegradability	100% Degradation After 21 Days	G. Müller/1992
Fishtoxicity (*Brachydanio Rerio*)	LC0 : 13.2 mg/l LC100 : 18.4 mg/l LC50 : 15.6 mg/l[1]	N. Caspers/1992
Bacteriatoxicity (Activated Sludge)	EC50 : 237 mg/l EC50 : 306 mg/l EC5 : 89 mg/l	G. Müller/1992 Bayer AG/1992

[1] Calculated

ACKNOWLEDGMENTS

The valuable contributions of Dr. Thomas A. Perfetti, R. J. Reynolds Tobacco Company, are gratefully acknowledged. I would like to thank Dr. Ian Gatfield and Dr. Manfred Köpsel for their assistance; Mrs. Angelika Sagebiel, Wilfried Bretschneider and Eberhand Zander for the drawings; and particularly Mrs. Ingrid Wengler for typing and layout of the manuscript.

REFERENCES

1. Alarie, Y. 1986. Summary report to the R. J. Reynolds Tobacco Company of sensory irritation studies. Toxicology Laboratory, Department of Industrial Environmental Health Sciences, University of Pittsburgh, Pittsburgh, Pennsylvania.
2. Bauer, K., Fleischer, J. and Hopp, R. 1971. Verfahren zur abtrennung von optisch reinem d- und l-menthol. German Patent 21 09 456.
3. Bauer, K., Garbe, D. and Surburg, H. 1988. Flavors and fragrances. Ullmann's Encyclopedia of Industrial Chemistry.

4. Bedoukian, P. Z. 1986. Menthol. Perfumery and Flavoring Synthetics. 3rd Edition. Allured Publishing Corporation, Wheaton, Illinois, pp 283-300.

5. BIBRA (The British Industrial Biological Research Association). 1990. Updated toxicity profile-menthol. Carsbalton, Surrey, GB.

6. Croteau, R. 1991. Metabolism of monoterpenes in mint (*mentha*) species. *Planta Medica 57,* Supplement Issue. 1:510-514.

7. Derfer, M. M. 1975. A literature survey on the physiological and pharmacological activity of menthol. SCM Glidden Organics, Jacksonville, Florida.

8. Dodt, E., Skouby, A. P. and Zotterman, Y. 1952. The effect of cholinergic substances on the discharges from thermal receptors. *Acta Physiologica Scandinacica.* 28:101-4.

9. Emberger, R. and Hopp, R. 1985. Synthesis and sensory characterization of menthol enantiomers and their derivatives for the use in nature-identical peppermint oils. Topics In Flavor Research. (R. G. Berger, S. Nitz and P. Schreier, Editors). H. Eichhorn, Marzling, Germany, pp 201-218.

10. Gildemeister, E. and Hoffmann, F. 1962. Pfefferminzöl. Die Ätherischen Öle (German). 4th Edition (W. Treibs, Editor). Akademie Verlag, Berlin, 7, pp 257-348.

11. Guenther, E. 1949. Oil of peppermint. The Essential Oils. D. Van Nostrand Company, Incorporated, New York, 3, pp 586-676.

12. Greenhalgh, P. 1979. The Markets for Mint Oils and Menthol. Tropical Products Institute, London, G 126.

13. Hattori, S., Komatsu, A. and Yamaguchi, Y. 1968. Method for the biochemical isolation of (-)-menthol. U. S. Patent 3,620,918.

14. Hellekant, G. 1969. The effect of menthol on taste receptors. *Acta Physiologica Scandinavica.* 76:361-368.

15. Hensel, H. and Zotterman, Y. 1951. The effect of menthol on thermoreceptors. *Acta Physiologica Scandinavica.* 24:27-34.

16. Hopp, R. and Mori, K., Editors. 1993. Recent Developments in Flavor and Fragrance Chemistry. Proceedings of the 3rd International Haarmann & Reimer Symposium. VCH Verlagsgesellschaft, Weinheim, pp 3-28.

17. Inoue, N. 1908. Japanische Pfefferminze (German). Bericht von Schimmel & Company, Miltitz, 2, pp 205-239.

18. Landgen, S., Skouby, A. P. and Zotterman, Y. 1953. Sensitization of baroreceptors of the carotid sinus by acetylcholine. *Acta Physiologica Scandinavica.* 29:381-388.

19. Landing, J. E. 1969. American Essence. A. M. Todd Foundation, Kalamazoo, Michigan.

20. Lawrence, B. M. and Shu, C. K. 1989. Peppermint oil differentiation. *Perfumer & Flavorist.* 14(6):21-30.

21. Lee, C. K. 1980. R. J. Reynolds Tobacco Company, Personal communication.

22. Leffingwell, J. C. and Shackelford, R. E. 1974. Laevo-menthol-syntheses and organoleptic properties. *Cosmetics and Perfumery.* 89(6): 69-89.

23. Litton Bionetics, Incorporated. 1975. Mutagenic evaluation of compound FDA 71-57, menthol. NTIS, PB-245 444, pp 152.

24. Misra, A. N., Soman, R. and Sukh Dev. 1988. *Monoterpenoids-VI.* On the optical purity of (+)-3-carene from *Pinas Roxburghii*, and the source of racemization of (-)-menthol derived therefrom. *Tetrahedron*. 44(22):6941-6946.

25. National Cancer Institute. 1979. Bioassay of d,l-menthol for possible carcinogenity. DHEW/PUB/NIH-79-1348, NCI-CG-TR-98; PB-288/761.

26. Opdyke, D. L. J. 1976. Fragrance raw materials monographs: menthol, menthone, menthyl acetate. *Food Cosmet. Toxicol.* 14:471-479.

27. Otsuka, S., Tani, K., Yamagata, T. and Akutagawa, S. 1981. Process for the preparation of enamines and imines. EU Patent 0068506.

28. Ray, J. 1696. Synopsis Methodica Stirpium Britannicarum. 2nd Edition. Smith and Walford, London, 124.

29. Schäfer, K., Braun, H. A. and Isenberg, C. 1986. Effect of menthol on cold receptor activity. Analysis of receptor processes. *Journal of General Physiology*. 88:757-776.

30. Schumacher, K. H. 1991. Optamint - freshness with taste to match. H&R Contact, Haarmann & Reimer GmbH, Holzminden, Germany, 52, pp 18-23.

31. Simonsen, J. L. and Owen, L. N. 1947. Menthol. The Terpenes. 2nd Edition. University Press, Cambridge, 1, pp 230-249.

32. Skouby, A. P. and Zilstorff-Pedersen, K. 1954. The influence of acetylcholine-like substances, menthol, and strychnine on olfactory receptors in man. *Acta Physiologica Scandinavica*. 32:252-258.

33. Skouby, A. P. and Zilstorff-Pedersen, K. 1955. The influence of acetylcholine, menthol, and strychnine on taste receptors in man. *Acta Physiologica Scandinavica*. 34:250-256.

34. Sukh Dev. 1978. New industrial processes based on carene. 11th IUPAC Int. Symp. Chem. Nat. Prod., (N. Marekov, I. Ogynyanov and A. Arahovates, Editors), 4(1), pp 443-447.

35. Swandulla, D., Schäfer, K. and Lux, H. D. 1986. Calcium channel current inactivation is selectively modulated by menthol. *Neuroscience Letters*. 68:23-28.

36. Takahashi, K., Someya, T., Muraki, S. and Yoshida, T. 1980. A new ketoalcohol, (-)-mintlactone, (+)-isomintlactone and minor components in peppermint oil. *Agricultural and Biological Chemistry*. 44(7):1535-1543.

37. Watson, H. R., Hems, R., Roswell, D. and Spring, D. J. 1978. New compounds with the menthol cooling effect. *J. Soc. Cosmet. Chem*. 29:185-200. (See references within).

38. Werkhoff, P. and Hopp, R. 1986. Isolation and gas chromatographic separation of menthol and menthone enantiomers from natural peppermint oils. Progress in Essential Oil Research (E. J. Brunke, Editor). Walter de Gruyter, Berlin/New York, pp 529-549.

39. Werkhoff, P., Brennecke, S. and Bretschneider, W. 1991. Progress in the chirospecific analysis of naturally occurring flavour and fragrance compounds (German). *Chem. Mikrobiol. Technol. Lebensm.* 13:129-152.

40. Werkhoff, P., Brennecke, S., Bretschneider, W., Güntert, M., Hopp, R. and Surburg, H. 1993. Chirospecific analysis in essential oil, fragrance and flavor research. *Z. Lebensm. Unters. Forsch.* 196:307-328.

REVIEW OF TECHNOLOGIES RELATING TO MENTHOL USE IN CIGARETTES

August J. Borschke

R. J. Reynolds Tobacco Company
Bowman Gray Technical Center
P. O. Box 1487
Winston-Salem, NC 27102

ABSTRACT

The patent art relating to the use of menthol in smoking articles for the period from 1924 through 1992 has been reviewed. The majority of the patent documents reviewed have been awarded to cigarette manufacturing companies. However, a significant number of patent documents also are owned by companies which supply materials or machinery for cigarette manufacture. Approximately 100 patent documents which have been reviewed have disclosed methods for applying menthol to tobacco, methods for incorporating menthol into smoking article components, and various menthol compositions. Typically, menthol is applied to tobacco by spraying solutions or dispersions containing menthol onto tobacco. Menthol has been incorporated into papers used to manufacture cigarettes, into cigarette rods and into cigarette filters. Menthol also has been incorporated into cigarette packaging materials. Menthol compositions often use precursor compounds which release menthol when cigarettes incorporating such compounds are smoked.

INTRODUCTION

This paper contains a review of those technologies pertaining to the use of menthol and related flavors in smoking articles, such as cigarettes. The technologies discussed in this paper are those which have been described in selected patent documents.

Individuals and corporations seek patent coverage because they believe that they have developed unique technologies. Because such individuals and corporations recognize the potential value of such unique technologies, they desire to take steps to prevent other individuals or corporations from employing similar technologies. Therefore, individuals and corporations can use patents to protect novel, commercially valuable technologies from being infringed upon by other individuals and corporations who have not been given permission to employ such technologies.

Patents can be obtained in many countries throughout the world. Each country has its own laws relating to procedures for obtaining patents and ways to enforce patents against infringers. In the United States of America, patents are legal documents which are used to prevent other individuals or corporations from making, using or selling inventions or discoveries which are new, useful and unobvious (1). The owner of a United States patent can enforce that patent against anyone who infringes that patent in the United States. A United States patent is enforceable for a period of 17 years from its date of issue (2). After a patent expires, the technology protected by that patent is free for the public to use.

Patents are a good source of technical information because each patent contains a disclosure of the technology which is intended to be protected. Each patent contains a written description of the patented invention sufficient to allow that invention to be made and used (3). Normally, patents contain at least one drawing along with a written description of the invention sought to be patented (4). Technologies described in patents can be machines, articles of manufacture, compositions of matter or processes (5).

Given that patents describe novel inventions or discoveries, patents can be used as effective tools in setting forth a historical perspective of the development of technology. That is, inventors who recognize unique and valuable technologies promptly describe their inventions in the patents that they receive. As such, when a fairly broad time frame of the patent literature for a selected technology is viewed, the chronology of events associated with the development of that technology can be observed.

This paper provides a review of the patent art for the period from 1924 through the end of 1992. The subject matter of that review relates to menthol and related flavors in smoking articles. Accordingly, 99 patent documents from the United States and several other countries are reviewed in this paper. Those patent documents are listed in the bibliography, which includes the patent number, the name of the inventor, the owner of the patent, the title of the patent and the year of issue of the patent.

Patent documents are discussed in this paper according to three categories. The first category relates to the application of menthol to tobacco, and includes a description of processing techniques and machinery used for incorporating menthol into tobacco. The second category relates to cigarette components incorporating menthol, and includes a description of various techniques for incorporating menthol into certain regions of cigarettes. The third category relates to chemical compositions including menthol, and includes a description of compositions which have a tendency to provide menthol flavor characteristics during smoking.

APPLICATION OF MENTHOL TO TOBACCO

The first patent relating to the application of menthol to tobacco for use in cigarettes was awarded to L. F. Hughes in 1925 (6). That patent described a process for treating tobacco for use in the production of cigarettes in order to provide cigarette tobacco which, when smoked, reportedly was cooling, soothing and pleasant to taste. The process involved spraying tobacco with a solution of menthol, cassia oil and alcohol. The tobacco so treated then was rolled into cigarettes.

Numerous references also suggest spraying menthol onto tobacco, particularly when the menthol is contained in a liquid carrier. One method involved spraying a mixture of water, ground tobacco and menthol onto tobacco filler (7). Another method involved spraying onto tobacco a menthol-containing casing composition incorporating glycerin and an organo-silicon compound (8). Another method for treating tobacco to form mentholated tobacco involved providing a mixture of menthol crystals, butylene glycol and water, and spraying that mixture over the tobacco (9). U. S. Patent No. 3,419,015, assigned to Hauni-Werke Korber & Company, K.G., contains a description of a method and apparatus for mixing casing and flavoring solutions with tobacco (10). Other techniques for contacting additives with tobacco have involved propelling a supply of tobacco through a zone in which a spray of finely dispersed additive is supplied (11). It also has been suggested that menthol can be dispersed in water, agitated using a high speed emulsifier, and sprayed onto tobacco (12). Further proposed techniques for applying menthol to tobacco involved spraying tobacco with an emulsion which included a mixture of menthol, ethanol, propylene glycol, malto-dextrin, modified corn starch, gum arabic, sorbitol laurate, collagen hydrolysate and water (13).

Attempts have been made to apply menthol to tobacco while that tobacco is in a moving stream. A solution of menthol and ethanol reportedly was applied to a moving stream of tobacco through a spray nozzle in a venturi area of a conduit through which the tobacco stream passes (14, 15). It also has been proposed to provide uniform absorption of menthol within tobacco by pneumatically conveying heated menthol vapor in an air stream in a conduit, and injecting tobacco into the conduit so as to allow contact of the tobacco and menthol streams (16). Yet another method involved spraying a controlled amount of menthol within a polyhydric alcohol carrier onto tobacco which fell through a tower (17, 18).

Certain attempts have been made to incorporate menthol into tobacco before that tobacco is processed or while that tobacco is being processed. As one example, menthol has been dispersed in liquid carbon dioxide which then was used to expand tobacco using the dry ice expanded tobacco (i.e., diet) process, so as to provide an expanded, mentholated tobacco (19). As a further example, mentholated tobacco rods have been subjected to conditions sufficient to expand the tobacco within those rods without significant loss of menthol (20). As yet another example, an extracted tobacco pulp has a predetermined amount of tobacco extract distributed within that pulp along with a controlled amount of menthol (21).

Attempts have been made to apply menthol to cigarette component materials as cigarettes are manufactured. It has been proposed to spray a solution of alcohol and menthol through a nozzle onto tobacco positioned on the suction belt of a cigarette maker just prior to the point in time that the tobacco is transferred to the garniture region of the maker (22). It also has been suggested to spray menthol onto tobacco accumulated on the suction belt of a cigarette making machine prior to the time that all of the tobacco to be transferred to the garniture region of the maker has accumulated on that belt (23). Foams containing menthol reportedly have been applied to tobacco at locations within the cigarette maker during cigarette manufacture (24). Philip Morris Incorporated has suggested adding menthol to a tobacco stream in the garniture region of a cigarette maker by passing menthol through a conduit formed in the short tongue of the maker (25).

There have been developments directed toward improvement in the quality of mentholated tobacco. For example, R. J. Reynolds Tobacco Company has developed an automated system utilizing a near infrared reflectance spectrometer in order to determine the amount of menthol in tobacco (26).

CIGARETTE COMPONENTS INCORPORATING MENTHOL

Menthol has been incorporated into cigarettes as an additive within certain components which are used to manufacture cigarettes. In this regard, menthol has been incorporated within the tobacco which makes up the tobacco rod of the cigarette, within the paper which is used to manufacture the cigarette, or within the cigarette filter. On numerous occasions, menthol is incorporated into certain cigarette components in order to minimize migration of menthol throughout the cigarette and to provide for controlled release of menthol during the smoking period. On other occasions, menthol is incorporated into certain regions of the cigarette in order that the menthol will migrate throughout the cigarette, and hence flavor the cigarette.

Various references have proposed incorporating flavors, such as menthol, within the paper which circumscribes the tobacco filler to provide the tobacco rod. Volatile flavorants reportedly were applied to cigarette paper as part of an encapsulating film-forming vehicle (e.g., a starch-based paste or a casein-based paste) (27). Cellulosic substrates (e.g., cigarette papers and tipping papers) were impregnated in anhydrous solutions of ammonia and menthol, and the ammonia was evaporated to yield menthol physically encapsulated within the cellulosic structure of the substrate for later release (28, 29). It also has been suggested that menthol could be entrapped in a film applied to plug wrap. Such a film was provided from a mixture of menthol, ethanol, triacetin and polyvinyl acetate (30). Cigarette papers reportedly have been printed with inks containing menthol and ethyl cellulose (31). It also has been suggested to incorporate menthyl glycosides into cigarette papers (32).

Carbon-containing papers have been reported to be effective in holding menthol until release is desired during the smoking period. Papers incorporating activated carbon, molecular sieves or polymeric microsponges reportedly hold menthol until those papers are subjected to elevated temperature conditions (33). Carbon filled inner paper wrappers for double wrapped cigarette rods reportedly have been used to hold menthol which is released by the heat of the burning zone of the cigarette during the smoking period (34). Another carbon-containing paper reportedly capable of carrying menthol includes activated carbon and magnesium hydroxide fillers (35). It has been suggested to incorporate activated carbon particles impregnated with menthol into a paper, which paper then is used as a component of a filter element (36). In addition, a gathered carbon-containing paper carrying menthol has been used as a flavor substrate segment for the mouthend region of a cigarette (37).

Numerous references have proposed incorporating flavors within coatings positioned at the extreme mouthends of cigarettes. As early as 1924, it was proposed that flavors such as peppermint could be incorporated into a water soluble coating applied to the mouthend tip of a cigarette (38). In that regard, the flavor was mixed with a paste provided from gelatin. In 1936, it was proposed that menthol could be employed with nitrocellulose and paraffin as a coating to the mouthend of cigarettes in order to provide a moisture proof region to those cigarettes (39). Menthol also has been suggested as a flavoring agent which could be incorporated into a flexible low density polyethylene tip for cigars (40).

Various techniques for incorporating menthol into cigarette filters have been proposed. It was suggested that finely divided menthol crystals could be incorporated into a fibrous mass in a tubular stem or holder for a cigarette (41). It also has been suggested to provide a cigarette holder with a central cavity for smoke passage which is filled with menthol crystals (42).

Certain cigarette filters have contained flavors which can be released prior to smoking in order to provide for transfer of flavor to mainstream smoke. As such, cigarettes incorporating such filters can be manipulated by the smoker to provide the desired delivery of menthol. One type of filter included an alginate encapsulated flavor which was positioned in a segment within the filter, and force applied by squeezing the filter reportedly released the flavor (43). Another type of filter included flavor-containing microcapsules, which flavor was disclosed as being released by the application of force to the filter (44). American Tobacco Company has proposed a method for incorporating menthol-containing microcapsules in a filter (45). Another cigarette mouthpiece included a sealed flavor-containing receptacle which reportedly could be moved to provide a smoke flow pathway in order to flavor that smoke (46). A rotatable filter had the capability to be adjusted to provide a selected amount of flavor to smoke passing through such a filter (47).

Numerous references contain disclosures which suggest that menthol can be combined with a carrier, and then incorporated into cigarette filters. Menthol incorporated into cigarette filters in such a manner reportedly tends to be held in place by the carrier, until the cigarette is smoked, when menthol then is transferred to the mainstream smoke. Such types of cigarette filters reportedly provide for increased cigarette shelf life as menthol tends not to migrate from the carrier, decreased loss of menthol in the sidestream smoke during the smoking period as the menthol is contained in the filter rather than the tobacco rod, and controlled delivery of menthol as the degree to which the carrier holds the menthol can be controlled. Menthol has been mixed with carbon particles, and the resulting menthol-containing carbon particles then have been placed in a cigarette filter (48, 49, 50). Menthol reportedly has been adsorbed to inorganic ion-exchange material (e.g., zirconium phosphate or hydrous titanium oxide) (51). It also has been suggested to provide magnesium silicate hydrate charged with menthol in a cigarette mouthpiece in order to aromatize smoke (52). Other types of cigarette filters containing magnesium silicate also have been proposed (53). Zeolite granules reportedly have been impregnated with menthol and incorporated into a cigarette filter (54). Granular activated carbon particles impregnated with pore modifying agents (e.g., sugar) and impregnated with menthol, reportedly provided for release of menthol from the filter during smoking (55).

Certain plastic materials incorporating menthol have reportedly been incorporated into filters. Plastic pellets impregnated with flavor have been incorporated into filters (56). It also has been proposed to wrap filter tow in a microporous polymer sheet (e.g., sheets of polypropylene or polyethylene) having flavor adsorbed therein in order to provide for release of flavor into mainstream smoke during the smoking period (57). Other cigarette filters reportedly have included flavor-carrying threads extending through the filter or flavor carrying-tape extending around the filter material (58).

Other types of filter materials have been suggested as potential carriers for menthol. Hollow fiber polyethylene filter materials reportedly have been impregnated with menthol and embedded within the filter plug (e.g., cellulose acetate tow) of a cigarette filter (59). Polyester fibers having a complex geometry have been suggested by Eastman Kodak Company to be cigarette filter materials capable of carrying flavorants for delivery during smoking (60). Polypropylene cigarette filter materials have been suggested as suitable carriers for menthol (61). Cigarette filters having inner core regions also have been suggested as being capable of retaining menthol during storage, while being capable of delivering menthol during the smoking period (62). It also has been proposed to incorporate menthol into an inner annular region of a cigarette filter manufactured from filter materials of different densities (63).

Menthol has been incorporated into the smokable material of the tobacco rod. It has been proposed to provide a filter cigarette having a mentholated tobacco rod and a filter incorporating a mixture of activated carbons in order to control the degree of menthol flavor present in mainstream smoke (64). It also has been suggested that menthol can be carried by an adsorbent substance (e.g., particles of activated charcoal, activated bauxite, alumina hydrogel or silica hydrogel) (65). Menthol encapsulated within gelatin or gum arabic to form heat rupturable capsules of 5 to 40 microns in diameter reportedly were incorporated into reconstituted tobacco or sprayed onto the tobacco leaf (66). Menthol also has been disclosed as being physically entrapped in a solid material and distributed within tobacco for uniform release of flavor during smoking. The solid material reportedly was a mixture of hydroxypropyl cellulose and gelatin, dextrin or gum acacia (67). It has also been suggested to incorporate menthol into a tobacco substitute (68). It has been suggested to sprinkle a mixture including crystalline menthol microcapsules over the tobacco of a cigarette (69). It also has been proposed to provide for a controlled concentration of menthol in mainstream smoke by providing menthol containing rupturable microcapsules in contact with tobacco filler (70). Suggested flavoring agents for tobacco also have included spray dried mixtures of menthol and gum arabic (71). Menthol crystals also have been incorporated into a high viscosity liquid strand which extends through a tobacco rod (72). Menthol has been encapsulated in an elongated ribbon-like capsule, and that capsule has been positioned within a tobacco rod (73). The use of the ribbon-like capsule reportedly provided for uniform release of the additive flavor during the smoking period. Philip Morris Incorporated has proposed incorporating filamentary flavor release material into a cigarette rod (74).

Besides being applied to cigarette components, menthol also has been applied to cigarette packaging materials. As such, it is reported that cigarettes packaged within such materials experience contact with menthol, and hence become mentholated, due to the migration of menthol from those packaging materials. In this regard, menthol has been applied to a traveling web of cigarette packaging material, and a menthol solution has been applied to the foil backed paper used for packaging cigarettes (75, 76). It also has been suggested to emboss a cigarette packaging material impregnated with a solution of menthol and alcohol (77).

Another method for providing menthol to packaged cigarettes involved incorporating within a cigarette package a wooden stick impregnated with menthol in order to provide for migration of menthol from the stick to the cigarettes (78). It also has been suggested to incorporate a menthol-containing tube resembling a cigarette into a cigarette package in order to provide menthol flavor to cigarettes within that package (79). In a similar vein, an applicator which allowed the smoker to apply menthol to individual cigarettes also has been proposed (80).

CHEMICAL COMPOSITIONS INCLUDING MENTHOL

Beginning in the 1960's, there were proposed various methods directed toward maintaining and preserving menthol during cigarette manufacture and storage. As a result, there exist numerous patents disclosing ways to control the volatility of menthol.

In the early 1960's, Brown & Williamson Tobacco Corporation developed several menthol-containing additives for tobacco products. The additives reportedly eliminated problems in manufacturing rooms associated with volatile menthol acting as a contaminant. In addition, the additives reportedly provided for a protracted shelf life to the mentholated tobacco product, as well as desirable menthol release into smoke upon smoking of the tobacco product. Certain menthol precursor additives included menthyl esters of polycarboxylic acids (e.g., monomenthyl maleates, monomenthyl succinnates and monomenthyl phthalates) (81). Other such additives included menthyl acetals (e.g., veratraldehyde methyl ethyl acetal and benzaldehyde dimethyl acetal) (82). Yet other menthol precursor additives have included menthyl ethers (e.g., menthyl phenyl ether and menthyl amyl ether) (83), and esters of menthol and organic keto acids (e.g., menthyl acetoacetate and menthyl levulinate) (84).

Numerous other attempts were made to provide menthyl esters, particularly during the 1960's and 1970's. Liggett & Myers Incorporated proposed several carbonate esters of menthol and polyhydroxyl compounds (e.g., monosaccharides, disaccharides, polysaccharides and glycols) (85, 86, 87). Philip Morris Incorporated investigated various polymeric carbonate esters of menthol, which were provided from monomers of carbonate esters of menthol (88, 89, 90). One example of a polymeric carbonate ester of menthol is 1-menthyl-1, 1-dimenthylallyl carbonate (91). Finely divided microporous polymers of divinylbenzene and styrene also have been suggested as carriers for menthol which then could be positioned in the filter region of a cigarette (92). Other flavor release compounds have been proposed. Compounds such as menthyl-2,3-dideoxy-D-erythrohexapyranoside can yield release of menthol upon pyrolysis (93). Another menthol release additive for cigarettes is comprised of a mixture of menthyloxy-carbonyl glucose compounds (94). In the 1960's, Philip Morris Incorporated investigated using inclusion complexes in order to provide for incorporation of menthol into a tobacco product as well as release of menthol when the product is smoked. Inclusion complexes were formed between a flavor compound and a host which held that flavor compound until exposure to elevated temperatures. One type of inclusion complex was comprised of menthol and alpha-cyclodextrin (95). Other inclusion complexes included cyclodextrin and tri-o-thymotide hosts (96). Beta-cyclodextrins also have been suggested as hosts for inclusion complexes containing menthol (97).

Certain attempts have been made to provide compounds which yield menthol or menthol-like notes or sensations. Certain references contain disclosures relating to the synthesis of such types of compounds (98, 99). Another reference discloses that 1-menthyl linalool carbonate as an additive to cigarettes provides for controlled release of menthol and citrus flavors during a smoking period (100). Other references suggest delivering menthol flavor along with lime or monellin (101, 102). Yet another reference suggests that 2-hydroxymethyl-menthol and 3-(beta-hydroxyethyl)-carvomenthol produce cooling sensations, and are useful flavoring additives in tobacco products (103). It also has been suggested to provide a menthol sensation to tobacco smoke by incorporating terpin hydrate into smoking tobacco (104).

SUMMARY

The majority of the patents relating to the use of menthol in smoking articles is owned by cigarette manufacturing companies, such as R. J. Reynolds Tobacco Company, Philip Morris Incorporated, Liggett & Myers

Incorporated and Brown & Williamson Tobacco Corporation. A significant number of patents relating to the use of menthol in smoking articles also is owned by suppliers of components for cigarette manufacture. In this regard, suppliers of cigarette paper (e.g., Ecusta Corporation and Kimberly-Clark Corporation), cigarette filters and filter materials (e.g., American Filtrona Corporation; Baumgartner Papier, S.A.; Eastman Kodak Company and Hoechst Celanese Corporation), cigarette flavoring agents (e.g., Firmenich S.A. and International Flavors & Fragrances Incorporated) and tobacco processing machinery (e.g., Hauni-Werke Korber & Company, K.G.) have been active in pursuing patent coverage for technologies relating to the use of menthol in smoking articles.

Although the use of menthol in cigarettes was suggested during the 1920's, significant efforts toward the development of patented technologies did not occur until the 1960's, as is evidenced by the data presented in Table I. Inspection of the data in Table I also leads one to conclude that there continues to be significant efforts directed toward the development of technologies associated with improving menthol cigarettes, the components of those cigarettes or the manufacture of those cigarettes.

TABLE I

Number Of Patent Documents Relating To The Use Of Menthol and Related Flavors In Smoking Articles Referenced In This Paper According To Decade Of Issue And Publication

Years	Number Of Patents
1920 - 1929	2
1930 - 1939	4
1940 - 1949	0
1950 - 1959	2
1960 - 1969	20
1970 - 1979	25
1980 - 1989	26
1990 - 1992	19

Numerous patent documents describe technologies concerning application of menthol to tobacco. Many of those documents describe techniques for spraying menthol-containing solutions or dispersions onto tobacco. Representative of such techniques are methods for spraying menthol-containing solutions or dispersions onto tobacco while the tobacco either is present in casing-type drums or cylinders, or has the form of a moving stream passing through a duct or conduit. Other technologies concerning application of menthol to tobacco have involved contacting the menthol with the tobacco in various regions of a cigarette making machine during cigarette manufacture. Technologies which have been developing relative to menthol application to tobacco have been directed toward improving the efficiency of the use of menthol by avoiding waste, avoiding contamination of manufacturing facilities resulting from escape of volatile menthol, applying controlled levels of menthol to tobacco and cigarettes, and providing uniform application of menthol to tobacco and cigarettes.

A large number of the patent documents reviewed in this paper describe technologies concerning cigarette components incorporating menthol. Menthol has been incorporated into papers used to manufacture cigarettes. As such, technologies directed toward minimizing migration of menthol throughout cigarettes have involved encapsulating or entrapping the menthol. Menthol also has been applied to tobacco or incorporated into a cigarette rod. Representative techniques for incorporating menthol into cigarette rods have involved the use of microencapsulated menthol, capsulized menthol and mentholated filaments. Menthol also has been incorporated in filter regions of cigarettes, either because of convenience considerations associated with applying menthol to filter materials or because of attempts to hold the menthol in place within the filter until the smoking period. In theory, it has been desirable to incorporate menthol into the filter regions of cigarettes in order to avoid loss of menthol from the tobacco rod during the smoking period, to provide cigarettes which exhibit good shelf life due to a propensity to resist loss of menthol, and to provide a controlled delivery of menthol into mainstream smoke. Techniques associated with menthol incorporation into cigarette filters have involved technologies relating to filter configurations, filter materials and filter additives.

Certain patent documents describe technologies concerning chemical compositions, and particularly those compositions resulting from the reaction or interaction of menthol with other chemical compounds. Many of the chemical compositions are precursor compounds which minimize to a great degree the volatility of menthol, but upon exposure of heat and/or moisture release menthol. As such, disadvantages associated with menthol migration throughout the cigarette and loss of volatile menthol reportedly can be minimized.

Attempts toward developing improved technologies associated with mentholated cigarettes appear to be continuing. Several reasons for the interest in pursuing patent coverage for technological developments relating to mentholated cigarettes can be postulated. One reason could be the commercial interest in mentholated cigarettes which results in companies associated with the tobacco industry allocating resources to research toward developing unique improvements to a popular product. Another reason could be the competitive nature of the industry, and consequently a desire by cigarette manufacturers to provide a high quality product which is popular among smokers. Yet another reason could be a desire by cigarette manufacturers to apply innovative technologies to develop products which can be manufactured efficiently and effectively using cost effective techniques.

As long as cigarette manufacturers remain competitive, continue to explore and improve their products, continue to apply new technologies to provide improved products, continue to view mentholated cigarettes as being popular among smokers and continue to be conscious of manufacturing products in a cost effective manner, it can be expected that cigarette manufacturers will continue to provide the environment and resources necessary to allow their employees to make inventions and discoveries. As long as competitive companies have employees making inventions and discoveries, it can be expected that those companies will be pursuing patent coverage. For this reason, it is reasonable to expect that the patent literature should continue to contain teachings of many new technologies directed toward mentholated cigarettes.

ACKNOWLEDGEMENTS

Appreciation is expressed to Ms. Bonnie Binkley and Ms. Helen Chung for their assistance in assembling reference materials for this paper. The help of Mr. Chuck Sherman of Brown & Williamson Tobacco Corporatio and Mr. James Schardt of Philip Morris Incorporated during the preparation of this paper is gratefully acknowledged.

REFERENCES

1. 35 U.S.C. §§ 101, 102, 103 and 154.

2. 35 U.S.C. §§ 154 and 271.

3. 35 U.S.C. § 112.

4. 35 U.S.C. § 113.

5. 35 U.S.C. § 101.

6. Hughes, L. F. 1925. Process of treating cigarette tobacco. U. S. Patent No. 1,555,580.

7. Sowa, F. J., Assigned to American Machine and Foundry Company. 1951. Smoking article. U. S. Patent No. 2,565,052.

8. Dean, S. W. 1961. Casing compositions. U. S. Patent No. 2,969,795.

9. Rosenberg, S., Assigned to Alles & Fisher, Incorporated. 1963. Process of treating tobacco and the resultant product. U. S. Patent No. 3,085,581.

10. Wochnowski, W., Assigned to Hauni-Werke Kober & Company. 1968. Method and apparatus for mixing additives with tobacco. U. S. Patent No. 3,419,015.

11. Berndt, W., et al., Assigned to Hauni-Werke Korber & Company. 1977. Method and apparatus for conditioning tobacco. U. S. Patent No. 4,054,145.

12. Crouse, W. E., *et al.*, Assigned to Loew's Theatres, Incorporated. 1985. Process for treating tobacco products with water-insoluble flavorants. EPO 140,670.

13. Holzner, G., *et al.*, Firmenich SA. 1988. Process for the aromatization of tobacco. U. S. Patent No. 4,785,833.

14. Key, III, R. L., *et al.*, Assigned to Liggett & Myers Incorporated. 1970. Applying menthol to tobacco in a pheumatic system. U. S. Patent No. 3,548,838.

15. Key, III, R. L., *et al.*, Assigned to Liggett & Myers Incorporated. 1972. Method of treating tobacco with flavorants in a pheumatic system. U. S. Patent No. 3,678,939.

16. Banks, J. F., Assigned to Brown & Williamson Tobacco Corporation. 1974. Deposition of menthol on tobacco. U. S. Patent No. 3,800,806.

17. Mays, C. D., *et al.*, Assigned to R. J. Reynolds Tobacco Company. 1984. Apparatus and process for treating tobacco. U. S. Patent No. 4,438,775.

18. Mays, C. D., *et al.*, Assigned to R. J. Reynolds Tobacco Company. 1984. Tobacco treatment process. U. S. Patent No. 4,449,541.

19. De La Burde, R. Z., *et al.*, Assigned to Philip Morris Incorporated. 1981. Method for uniform incorporation of additives into tobacco. U. S. Patent No. 4,243,056.

20. White, J. L., *et al.*, Assigned to R. J. Reynolds Tobacco Company. 1990. Process for the manufacture of tobacco rods containing expanded tobacco material. U. S. Patent No. 4,962,773.

21. Fagg, B. S., *et al.*, Assigned to R. J. Reynolds Tobacco Company. 1992. Tobacco processing. U. S. Patent No. 5,131,414.

22. Ernow, S. A., Assigned to Svenska Tobaks Aktiebolaget. 1974. Method of producing cigarettes or the like filled with tobacco containing one or more aromatic liquid agents, and a device for carrying out the method. U. S. Patent No. 3,817,258.

23. Lettau, K. D., Assigned to R. J. Reynolds Tobacco Company. 1991. Process and apparatus for producing aromatized strand-shaped smoking material. U. S. Patent No. 4,995,405.

24. Albertson, D. E., et al., Assigned to Philip Morris Incorporated. 1986. Tobacco processing. U. S. Patent No. 4,619,276.

25. Nichols, W. A., Assigned to Philip Morris Incorporated. 1983. Method for applying particulate matter to tobacco. U. S. Patent No. 4,409,995.

26. Dominguez, L. M., et al., Assigned to R. J. Reynolds Tobacco Company. 1990. On-line tobacco evaluation system and method. U. S. Patent No. 4,971,077.

27. Keaton, J. L., Assigned to R. J. Reynolds Tobacco Company. 1961. Additives for smoking tobacco. U. S. Patent No. 3,066,347.

28. Rainer, N. B., et al., Assigned to Philip Morris Incorporated. 1978. Process for incorporating flavorant into cellulosic substrates and products produced thereby. U. S. Patent No. 4,123,592.

29. Rainer, N. B., et al., Assigned to Philip Morris Incorporated. 1980. Process for incorporating flavorant into cellulose substrates and products produced thereby. U. S. Patent No. 4,184,495.

30. Nichols, W., et al., Assigned to Philip Morris Incorporated. 1987. Matrix entrapment of flavorings for smoking articles. U. S. Patent No. 4,715,390.

31. Adams, B., et al., Assigned to Gallaher Limited. 1988. Process for producing smoking rod wrapper and smoking rod containing same. U. S. Patent No. 4,784,163.

32. Herron, J., Assigned to P. H. Glatfelter Company. 1989. Tobacco product containing sidestream smoke flavorant. U. S. Patent No. 4,804,002.

33. Cartwright, W. F., et al., Assigned to Kimberly-Clark Corporation. 1992. Flavor release material. U. S. Patent No. 5,144,967.

34. McCarty, S. W., et al., Assigned to Olin Corporation. 1973. Carbon filled wrapper for smoking article. U. S. Patent No. 3,744,496.

35. Owens, Jr., W. F., Assigned to P. H. Glatfelter Company. 1992. Wrapper for smoking article, smoking article, and method of making same. U. S. Patent No. 5,107,864.

36. Assigned to American Tobacco Company. 1964. Improvements in tobacco smoke filter element. G. B. Patent No. 951,510.

37. **Perfetti, T. A., *et al.*, Assigned to R. J. Reynolds Tobacco Company. 1992. Smoking article with improved means for delivering flavorants. U. S. Patent No. 5,137,034.**

38. **Marshall, Jr., H. H. 1924. Cigarette. U. S. Patent No. 1,507,925.**

39. **Sulzberger, N. 1936. Moisture proof cigarette and process of making same. U. S. Patent No. 2,033,791.**

40. **Laporte, L. C., Assigned to Imperial Tobacco Company of Canada. 1971. Cigar holder. U. S. Patent No. 3,589,371.**

41. **Banks, M. S. 1934. Smoking appliance. U. S. Patent No. 1,952,352.**

42. **Edison, R. G. 1980. Menthol filter for cigarettes. U. S. Patent No. 4,227,540.**

43. **Tateno, A., *et al.*, Asigned To Japan Tobacco Incorporated. 1989. Filter for tobacco smoking. U. S. Patent No. 4,889,144.**

44. **Veluz, S. E., Assigned to Baumgartner Papiers S.A. 1985. Aromatized cigarette filter. Switzerland Patent No. 648,733.**

45. **Wartman, W. B., *et al.*, Assigned to American Tobacco Company. 1970. Method of making a composite filter. U. S. Patent No. 3,550,508.**

46. **Keritsis, G. C., Assigned to Philip Morris Incorporated. 1991. Container for additive materials for smoking articles. U. S. Patent No. 4,991,605.**

47. **Kallianos, A. G., *et al.*, Assigned to Philip Morris Incorporated. 1987. Filter cigarette. U. S. Patent No. 4,677,995.**

48. **Lassiter, F. H., *et al.* 1964. Cigarette. U. S. Patent No. 3,150,668.**

49. **Irby, Jr., R. M. *et al.*, Assigned to the American Tobacco Company. 1966. Tobacco smoke filter element. U. S. Patent No. 3,236,244.**

50. **Stoneburner, G. R., Assigned to Calgon Corporation. 1975. Adsorbent carbons. G. B. Patent No. 1,382,476.**

51. Hiroshi, M., et al., Assigned to the Japan Tobacco & Salt Public Corporation. 1982. Flavorant composition for tobacco, method for producing the same tobacco product comprising said composition. U. S. Patent No. 4,318,417.

52. Bonnet, J., et al., Assigned to Baumgartner Papiers, S.A. 1982. Method for aromatizing tobacco smoke. U. S. Patent No. 4,311,156.

53. Phelpstead, J. W. P., Assigned to British-American Tobacco Company Limited. 1989. Smoking articles. U. S. Patent No. 4,838,286.

54. Green, J. D., Assigned to British-American Tobacco Company Limited. 1987. Smoking articles. U. S. Patent No. 4,662,384.

55. Tiggelbeck, D. D., Assigned to Calgon Corporation. 1976. Mentholated cigarette filter. U. S. Patent No. 3,972,335.

56. Greene, Jr., C. C., et al., Assigned to R. J. Reynolds Tobacco Company. 1989. Rods containing pelletized material. U. S. Patent No. 4,862,905.

57. Woods, D. K., et al., Assigned to R. J. Reynolds Tobacco Company. 1988. Microporous materials in cigarette filter construction. U. S. Patent No. 4,729,391.

58. Bynre, S. W., et al., Assigned to American Filtrona Corporation. 1981. Production of tobacco smoke filters. U. S. Patent No. 4,281,671.

59. Deutsch, L. J., et al., Assigned to Hoechst Celanese Corporation. 1990. Filter for a smoking article containing a flavored hollow fiber. U. S. Patent No. 4,971,078.

60. Mathis, D. E., et al., Assigned to Eastman Kodak Company. 1992. A combination for improved delivery of tobacco modifying agents. PCT WO92/05713.

61. Cohen, R. R., et al., Assigned to Hercules Incorporated. 1991. Method and device for control of by-products from cigarette smoke. U. S. Patent No. 5,038,803.

62. Rutherford, H. J., Assigned to International Flavors & Fragrances Incorporated. 1991. Method for imparting functional ingredients, functional ingredient-imparting articles and methods for preparation and use thereof. U. S. Patent No. 5,069,231.

63. Thesing, R. A., et al., Assigned to Philip Morris Incorporated. 1991. Flavored cigarette filters, and methods and apparatus for making same. U. S. Patent No. 5,012,829.

64. Lassiter, F. H., et al. 1965. Cigarette. U. S. Patent No. 3,169,535.

65. Allen, R. P., 1936. Tobacco. U. S. Patent No. 2,063,014.

66. McGlumphy, J. H., et al., Assigned to the National Cash Register Company. 1970. Reconstituted tobacco containing adherent encapsulated flavors and other matter. U. S. Patent. No. 3,550,598.

67. Marmo, D., et al., Assigned to International Flavors & Fragrances Incorporated. 1981. Process for augmenting or enhancing the aroma or taste of smoking tobacco or a smoking tobacco article by adding thereto a suspended flavoring composition. U. S. Patent No. 4,253,473.

68. Carroll, R. G., Assigned to Profair Corporation. 1968. Tobacco substitute. U. S. Patent No. 3,369,551.

69. Makajima, M. 1991. Agent for removing noxious tobacco components. U. S. Patent No. 5,000,198.

70. Taskino, L. M., et al., Assigned to Imperial Group Limited. 1974. Cigarettes and method of providing them with a flavorant. G. B. Patent No. 1,349,537.

71. Assigned to L. Givaudan & Cie, Societe Anonyme. 1977. Flavoring agent. G. B. Patent No. 1,472,737.

72. Haws, L. A., et al., Assigned to Philip Morris Incoporated. 1991. Cigarette rods with liquid flavor centers. U. S. Patent No. 4,993,434.

73. Moll, Jr., C. J., Assigned to Brown & Williamson Tobacco Corporation. 1964. Smoking articles having encapsulated tobacco additives and their manufacture. U. S. Patent No. 3,162,199.

74. Washington, J. M., Assigned to Philip Morris Incorporated. 1992. Filamentary flavorant-release additive for smoking compositions. U. S. Patent No. 5,144,966.

75. Scales, J. T., Assigned to Imperial Group Limited. 1975. Impregnation of a traveling web. U. S. Patent No. 3,906,893.

76. Kopachkov, S. A., Assigned to Rothmans of Pall Mall Canada Limited. 1978. Machine for applying liquid to absorbent material. U. S. Patent No. 4,068,614.

77. Gould, A., Assigned to Carreras Limited. 1972. Method of treating a wrapper and a packing method incorporating such wrappers. Canadian Patent No. 899,172.

78. Blank. M., *et al.* 1935. Cigarette flavoring device and process of making same. U. S. Patent No. 2,007,632,.

79. Rudiger, E. 1971. Menthol container for self impregnation of cigarettes. Fed. Rep. Germany No. 1,959,102.

80. Canan, W. T. 1963. Means for introducing flavor imparting agents into tobacco and tobacco articles. U. S. Patent No. 3,105,499.

81. Jarboe, C. H., Assigned to Brown & Williamson Tobacco Corporation. 1963. Smoking tobacco product and method of making the same. U. S. Patent No. 3,111,127.

82. Jarboe, C. H., *et al.*, Assigned to Brown & Williamson Tobacco Corporation. 1964. Smoking tobacco additives in the form of menthyl acetals. U. S. Patent No. 3,126,012.

83. Jarboe, C. H., *et al.*, Assigned to Brown & Williamson Tobacco Corporation. 1964. Smoking tobacco additives in the form of menthyl ethers. U. S. Patent No. 3,128,772.

84. Jarboe, C. H., Assigned to Brown & Williamson Tobacco Corporation. 1964. Smoking tobacco product having menthyl keto ester additive. U. S. Patent No. 3,136,319.

85. Mold, J. D., et al., Assigned to Liggett & Myers Tobacco Company. 1967. Tobacco incorporating carbonate esters of flavorants. U. S. Patent No. 3,332,428.

86. Mold, J. D., *et al.*, Assigned to Liggett & Myers Incorporated. 1968. Carbonate esters of flavorants. U. S. Patent No. 3,419,543.

87. Kallianos, A. G., *et al.*, Assigned to Liggett & Myers Incorporated. 1970. Tobacco compositions incorporating novel esters of polyhydroxy compounds. U. S. Patent. No. 3,499,452.

88. Rundberg, Jr., E. G. S., et al., Assigned to Philip Morris Incorporated. 1977. Smoking compositions incorporating a menthol-release agent. U. S. Patent No. 4,002,179.

89. Van Auken, T. V., et al., Assigned to Philip Morris Incorporated. 1979. Smoking tobacco compositions. U. S. Patent No. 4,177,339.

90. Van Auken, T. V., et al., Assigned to Philip Morris Incorporated. 1980. Unitary pack of smoking tobacco products containing polymeric alcohol flavorant-release compositions. U. S. Patent No. 4,212,310.

91. Rundbert, Jr., E. G. S., et al., Assigned to Philip Morris Incorporated. 1975. Menthol-release compounds. U. S. Patent No. 3,887,603.

92. Badgett, C. E., Assigned to Philip Morris Incorporated. 1971. Flavor-releasing smoking article and method of making same. U. S. Patent No. 3,603,319.

93. Christenson, P. A., et al., Assigned to K & F Corporation. 1990. Novel menthyl pyran compounds. EPO 389,945.

94. Chan, W. G., Assigned to Philip Morris Incorporated. 1992. Smoking compositions containing a menthol-release additive. U. S. Patent No. 5,139,034.

95. Bavley, A., et al., Assigned to Philip Morris Incorporated. 1962. Smoking composition. U. S. Patent No. 3,047,431.

96. Bavley, A., et al., Assigned to Philip Morris Incorporated. 1966. Composition for incorporating flavor into tobacco smoke. U. S. Patent No. 3,288,146.

97. Demain, B. A., Assigned to Philip Morris Incorporated. 1992. Smoking compositions containing a flavorant-release additive. U. S. Patent. No. 5,144,964.

98. Roberts, D. J., et al., Assigned to R. J. Reynolds Tobacco Company. 1968. Tobacco product. U. S. Patent No. 3,380,456.

99. Van Auken, T. V., Assigned to Philip Morris Incorporated. 1982. Synthesis of n-t-butyl-p-menthane-3-carboxamide. U. S. Patent No. 4,350,832.

100. Bavley, A., et al., Assigned to Philip Morris Incorporated. 1967. Smoking tobacco composition. U. S. Patent No. 3,312,226.

101. Van Der Loo, H. E., *et al.*, Assigned to Tate & Lyle Limited. 1981. Smoking articles containing thaumatin or monellin. G. B. Patent No. 1,604,217.

102. Aulbach, P. L., *et al.*, Assigned to British-American Tobacco Company. 1972. An improved smokable tobacco product. South Africa No. 72/3609.

103. Humbert, F. E. L., *et al.*, Assigned to Lever Brothers Company. 1977. *Compositions containing compounds* producing a cooling sensation. U. S. Patent No. 4,029,759.

104. Norton, S. G. 1952. Tobacco. U. S. Patent No. 2,586,701.

A HISTORY OF MENTHOLATED CIGARETTES
"THIS SPUD'S FOR YOU"

Jack R. Reid

Lorillard Tobacco Company
Research Center
P.O. Box 21688
Greensboro, NC 27420

ABSTRACT

In the late 1920's, *Spud* (the first mentholated cigarette) was marketed. Following early entries of *Penguin* and *Kool* brands in the 1930's, the market share maintained a consistent 2% up until the introduction of filters in the mid 1950's. *Salem*, then other, filtered mentholated cigarettes were offered to the public, and the market share of mentholated cigarettes increased, finally reaching a peak of about 30% in the mid 1970's. Currently mentholated cigarettes account for about 25% of the total cigarette sales.

INTRODUCTION

I have a lot of slides, mostly of cigarette pack designs, that I will be showing rather rapidly. The large number of beautiful pack designs, and interesting advertisements, made the selection of which to present extremely difficult. I sincerely apologize if I have, by this selection process, left out someone's favorite piece of nostalgia. I have tried to represent a balance of different manufacturers, different years of introduction, and radically different visual designs. So sit back, relax, and let's go back to the late 1920's for the beginning of the mentholated cigarette.

THE BEGINNING - THE TORRID TWENTIES

Mentholated cigarettes were developed in quite an unusual way. A young man who suffered from chronic colds, placed his treatment dosage of menthol crystals, prescribed by his mother, into a baking powder tin, along with his favorite smoking tobacco. He allowed the two materials to remain sealed together overnight. The next morning, as he rolled his cigarettes for that day, he lit one and found that he had created the first mentholated cigarette. For the first time, he was able to tell his mother that he had willingly used his menthol treatments. It is suspected that he avoided mentioning that, at the same time, he also was able to enjoy his favorite cigarette tobacco.

The young man was Lloyd F. Hughes, known by the nickname of "Spud" Hughes. Spud worked in his father's restaurant in Mingo Junction, Ohio, a small town on the Ohio River about 20 miles north of Wheeling, West Virginia. He began by offering his new cigarettes to the railroad men and mill workers who frequented his father's establishment. The instant popularity of this new cigarette required him to roll increasingly more cigarettes each day as gifts. At that point he decided to try selling his new creation. With the help of a friend, Spud further refined his process. He applied for, and was granted, a patent for the process of treating tobacco with menthol (3).

When the cigarette began to be successful, Spud gave up his job in the restaurant and set out for fame and fortune. What name did he choose for his new cigarette? What else - *Spud*. He got married, moved to Bridgeport, Ohio and then to Wheeling, West Virginia, where his father-in-law, the chauffeur of one of the city's millionaires, gave him a place to work and sleep. During this time he continued to improve his mentholation process. He signed a contract with Bloch Brothers Tobacco Company, makers of *Mail Pouch* chewing tobacco, to manufacture *Spud*. Once each week he arrived at the factory and performed his mentholation process with a pitchfork and hand-sprayer.

The popularity of the new cigarette concept increased and he began to make a lot of money, as word of his new cigarette spread. In May 1926, in his basement home, he formed a company known as the Spud Cigarette Corporation. Bloch Brothers was still doing the bulk of the manufacturing for him. His corporation had three employees: Spud, the President and main cigarette salesman; his wife, stenographer, secretary, package handler, and shipping clerk; and within a year, his father, Thomas Hughes, cigarette salesman. Mr. Hughes had quit the restaurant business to join Spud for a more lucrative opportunity. The three were able to make a decent living from the volume of local sales Spud had established.

Spud did not let the grass grow under his feet for long. His newfound wealth became addictive and he began to canvass tobacco companies with larger facilities to manufacture increased quantities of *Spud* cigarettes. The Axton-Fisher Company agreed to manufacture the cigarettes in the summer of 1926 and became the chief supplier of these cigarettes. This arrangement lasted several months, then Colonel Woodford Axton, a colorful character in his own right, offered to buy out the Spud Cigarette Corporation.

Colonel Axton felt that the cigarette could be much more profitable if handled correctly. Before the advent of 10¢ per pack brands, the 20¢ per pack *Spud* was already outselling the 15¢ per pack premium brands, with the exception of *Lucky*

Strikes, *Camels*, *Chesterfields*, and *Old Golds*. The Axton-Fisher Company made the offer for outright purchase of the *Spud* brand. Spud Hughes agreed and the sale was finalized after a transfer of $90,000 cash to Spud in person. Spud was out of the *Spud* cigarette business.

Before following the *Spud* cigarette once it was turned over to Colonel Axton, I would like to pursue what happened to Spud Hughes, after selling his cigarette brand, as an insight into his character. Spud divided the money between himself and his father. The lure of this exorbitant amount of money was too great for him. Not noted for being a completely responsible young man, he went on a wild spending spree. A day or so later, Spud went to Cincinnati, where he bought a new Waco biplane. The company, fearing liability problems, would not let him fly it immediately, since he had no flight experience. However, he convinced a friend, a former Army flier, to get him started. Once in the air, he took over the controls, overshot the field on landing and with all the skill of a ground dweller, smashed it into a slag pile near the end of the runway. Discouraged? Not on your life. He had the plane repaired and managed to land it without serious incident later that week. Encouraged by this limited success, he spent the money to open an airport in Yorkville, Ohio, and went barnstorming throughout the state for the next two years.

Within two years, Spud had completely smashed no less than six airplanes. A spectacularly devastating crunch into the side of a mountain in Pennsylvania was closely followed by totalling a new airplane on a hillside in Ohio, when he tried to land at night, in fog, using only a flashlight. The amazing part of his entire airborne, or violently grounding, experiences is that the only personal damage he sustained was the loss of several front teeth. Airplane breakage and declining sales of Waco biplanes forced him to sell the airport in 1928. Money depleted, he got a job, first as a filling station attendant, then as a postman. When last seen he had packed up his wife and they were headed toward Hahira, Georgia, in an attempt to make and sell *Julep*, a cigarette with a Mint Julep taste. Spud Hughes was not heard from again (7). The *Julep* cigarettes, however, were marketed first by the Julep Cigarette Company, located in Boston, then later, in a redesigned cigarette pack, by Brown & Williamson. The relationship of these companies with Spud Hughes is unknown.

I would like to make a small digression concerning Colonel Axton. Colonel Axton's approach to business was radically different from that of Spud Hughes. Originally a grocery salesman, he accepted some tobacco-making equipment as payment for an outstanding debt of $60. Thus, he began to sell tobacco products under his own name. His brands were popular in the small communities around his immediate area, but he did have some trouble with other manufacturers. The Tobacco Trust was giving the Axton Tobacco Company problems with their new lower-priced cigarettes and arrogantly aggressive sales force.

Here are two short stories to give you some insight into Woodford Axton's character. Axton-Fisher's short lived *Clown* cigarette (1921-1924), appeared during the time of the Tobacco Trust troubles. The pack design, in which a girl dressed as a clown sticks her head through a very familiar bull's eye, was conjectured, by persons at that time, to be a rude gesture directed at American Tobacco Company's Lucky Strike. While not actually violating the existing tobacco regulations he skirted the edge of legality, possibly to make a point. In the 1930's, the Axton-Fisher Company sold *Head Play*, an 11 inch cigarette that took advantage of a tax loophole. It was a novelty item for three years, until the loophole was closed (4).

Through personal contact and his neighborly approach, Colonel Axton was able to maintain local sales and actually increase distribution of his products. As business grew, he took on a partner, George H. Fisher, to run the plant while he was on the road as salesman. The company became the Axton-Fisher Tobacco Company. Business was still confined to a relatively small sales region.

Now we return to *Spud*, the mentholated cigarette. Word of *Spud* continued to spread. Under the watchful eye of Colonel Axton, the cigarette was launched nationwide in

December of 1926. Profits did indeed increase, but the Colonel ran into a problem he hadn't expected. At first, distribution was very segmented and completely inadequate for the unprecedented demand. People besieged the stores looking for the new brand and retailers predicted a deluge of orders.

The Axton-Fisher Company responded, by diverting resources toward the production of *Spud*, thus dramatically increasing their cigarette output. Soon the retailers were completely stocked, and sat around waiting for the predicted deluge to hit. Unfortunately, it never materialized as expected, and much of the stock sat on the retailers' shelves, rapidly deteriorating in quality. The retailers, of course, sold their older stock first, so the product distributed to the smoking public began to taste worse and worse. The resulting poor quality of product distributed to the general public, and the previous supply problem, brought the reputation of the brand into disrepute.

During 1927, *Spud* was a big disappointment to the Axton-Fisher Company. In 1928 the Axton-Fisher Company, needing capital, broke its long-standing policy of private ownership and sold $1,000,000 of common stock, thus acquiring banking connections in New York. With the new capital, the company refurbished its old plant and built an additional modern processing area. On one trip to New York, Colonel Axton met with some advertising executives, who convinced him of the benefits that could be gained by promoting his products through the media. A combination of judicious advertising and an eye on quality brought the brand back into favor and sales increased up through the year 1930.

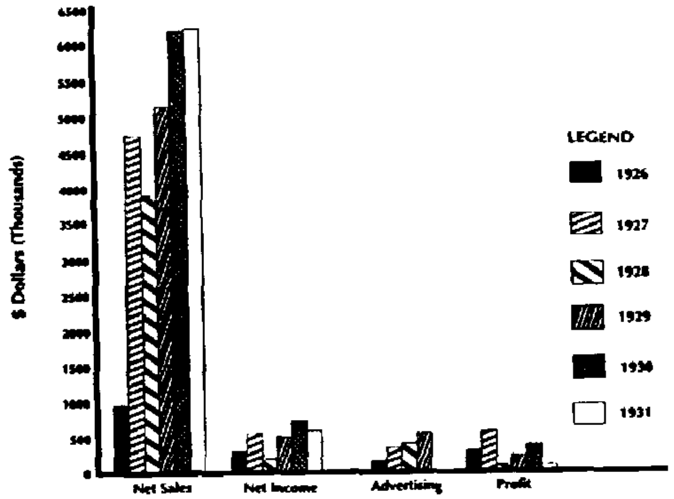
The years of the Depression, 1929-1932, were dangerous times for cigarette companies. By the end of 1932, 20% of the total U. S. cigarette market was occupied by the *ten-centers*, the new 10¢ per pack brands, as sales of the then dominant 15¢ packs dropped by 10 billion units. There was an equivalent rise in *roll-your-own* brands as the 15¢ per pack brands lost volume. The *ten-center* was able to be offered as a cheaper alternative because of the general fall in leaf prices, along with what was called "sensible economies" in advertising and packaging.

THE THREAD-BARE THIRTIES

The majority of the advertising money that Axton-Fisher spent in the period 1928-1931 was for the *Spud* cigarette brand. Trying to devise advertising copy for a cigarette brand with a name connoting a potato must have been challenging. The depression was in full swing and the year 1931 saw a drastic decrease in profits. Adding to this, the Brown & Williamson Tobacco Company had introduced *Penguin* mentholated cigarettes in 1931; then as time progressed, they introduced *Kool Menthol* in 1933. As a result, *Spud* lost additional market share (5).

Figure 1 summarizes the published facts, but does not tell the whole story.

FIG. 1
Axton-Fisher Company
1926 - 1931



In the late 1930's, the Axton-Fisher Company was taken over by Philip Morris Incorporated. Under the new leadership of Philip Morris, *Spud* held onto a small segment against *Kool*. The cigarette *Spud* was destined to hold its own until its eventual dissolution in 1963. The mentholated cigarette market sustained a relatively static 2% market share from the late 1930's up until the early 1950's.

This was not the first time treated cigarettes were to be offered to the smoking public. In 1927, *Listerine* cigarettes were sold (Lambert Pharmaceutical Company) in which the tobacco had been impregnated with antiseptic oils. Another presentation included *Eucalyptus*, an essential oil treated cigarette. The menthol treatment, however, was eminently more successful. During this time, numerous companies developed their own versions of a mentholated product and new mentholated brands were introduced. Some of these include the previously mentioned *Penguin* in 1931 (Brown & Williamson), *Snowball* (Paul A. Werner, New York), the phenomenally successful *Kool* in 1933 (Brown & Williamson), *Cigarette-Time* (Philip Morris), and *Menthorettes* (Rosedor Cigarette Company).

THE FANTASTIC FORTIES

The era of increasing economic prosperity, beginning with the start of World War II, had a positive effect on the tobacco industry. In spite of leaf shortages and long waiting lines outside tobacco shops, the war years encouraged consumption. Tobacco was classified as an essential material by President Roosevelt, and some tobacco farmers won deferments from military service. Between 1939 and 1945, cigarette sales in general rose by 50%, and manufacturers faced peacetime with a known demand for nearly 270 billion cigarettes at home. This demand increased even more after the war, since the returning servicemen had taken 18% of the total output, for overseas supply, during the war years (1).

The use of mentholated products was initially promoted to offer an alternative to the heavy, harsh-tasting, hot, and many times unpleasant experience of some nonmentholated products. The trend was to offer these mentholated cigarettes as a change-of-pace product, particularly as a "refreshment" cigarette during the winter months when lowered indoor humidity was thought to contribute to dry throats.

THE FILTER FIFTIES

Filter cigarettes were developed and introduced in the mid 1950's, and came to dominate the market. A spate of new filtered menthol brands were introduced, reflecting the positive image of cooling and reduced harsh-tasting tobaccos.

The addition of a filter to regular cigarettes changed the stronger tobacco tastes to which many smokers had become accustomed. Thus, there was already a need for flavoring to compensate for this loss of tobacco flavor. In its rise, the filter market absorbed and enlarged the once limited demand for mentholated cigarettes. In spite of the *Spud* brand introduced in 1926, this market, like the *mouthpiece* market, remained small for many years. Only Brown & Williamson's *Kool*, offering prize coupons along with menthol flavoring, managed to achieve any kind of volume as a mentholated nonfilter cigarette (12,700,000,000 by 1955). The popularity of filters, the long-term association of menthol with a cool refreshing taste, and the growing popularity of *Kool*, a nonfiltered, mentholated cigarette, undoubtedly prompted the introduction of *Salem*, the first menthol filter cigarette, in May, 1956 by R. J. Reynolds. National distribution was attained a month later (2, 6).

In response to Reynolds' invasion of the menthol market, Brown & Williamson immediately placed a filter on its regular sized *Kool* brand and put it on the market later in 1956. Although Brown & Williamson had good success with its regular (nonfilter) *Kool Menthol* brand, it apparently had been uncertain as to the strength and direction of the filter trend versus the nonfiltered king size trend for cigarettes. As a result, it offered a king size version of its popular, regular sized *Kool Menthol* brand in 1953, instead of the filtered version. The king size brand was discontinued in 1956, when the *Kool Menthol Filter* was introduced.

Other entries into the menthol filter market included *Newport* (Lorillard) and *Oasis* (Liggett & Myers) in 1957, and Lorillard's *Sprint 100's* and Philip Morris's *Alpine Menthol Filter* brands in 1959. By the end of 1958, mentholated brands accounted for about one out of every six filter cigarettes smoked, or one out of every twelve cigarettes of all types.

THE SALIENT SIXTIES

Brown & Williamson responded in 1960 with *Belair Menthol Filter*, followed closely by *Montclair Menthol Filter* from the *American Tobacco Company* in 1962. The menthol filter market seemed to reveal that first entry may be associated with substantial, but not everlasting success. For sixteen years, *Salem* maintained the leading position in the menthol filter market, but in 1972 it was overtaken by *Kool*. *Kool's* lead continued on through 1979, despite large increases in advertising expenditures by *Salem*.

Kool's ascendancy cannot be explained by the amount of dollars spent to advertise the brand. Except for 1971, *Kool* spent less on advertising than did *Salem* throughout the 6 year span of the 1968-1974 period. Possibly *Kool's* success indicates that it had a more effective advertising campaign than did *Salem*. Another possibility was that according to the 1969 Maxwell report, *Kool* was then the most heavily mentholated of all the mentholated cigarette brands (9), and this was the preferred taste of that era.

Initially, mentholated products and associated advertising campaigns were developed based upon the feedback received from the smoking public in general. The lack of response, evidenced by the essentially flat sales volume, caused the advertising agencies to use a different approach. Companies responded with a proliferation of visually appealing advertising and new packs targeted to appeal directly to the menthol smoking public. Since 1962, mentholated counterparts of brand releases have been taken for granted. In almost every case, when a new brand is currently released, there is a mentholated version developed and released as well to capture that segment of the smoking public which prefers this taste mixed with its tobacco.

THE SCHISMATIC SEVENTIES

In the seventies, markets began to level off. Sales stabilized at about 27% to 30% of the total cigarette market, and advertising continued to change with the needs of the customers. A proliferation of additional brands was introduced, many of which were discontinued within two to three years.

THE EIGHTIES AND NINETIES

While some initial experimentation was done to find the most desirable levels of menthol, the levels of menthol have changed very little over the years. Some 90% of all cigarettes contain a very small amount of menthol. This supplement merely enhances the tobacco tastes, without the minty, cooling components of menthol taste being noticeable. Mentholated cigarettes contain from 0.3% to 0.7% of the tobacco weight in menthol, with the range extending to nearly 1% for highly-mentholated cigarettes. While menthol cigarettes today do not account for more than 1% to 5% of the market in most countries, the total is greater than 25% in the United States. In the Philippines, menthol cigarettes account for more than 60% of the market (8).

The three largest menthol brands through the seventies and on into the nineties were *Salem*, *Kool*, and *Newport*. In the early seventies *Kool* passed *Salem* as the brand leader. This lasted for approximately 10 years. Reynolds' *Salem* brand then recaptured its position as the leader. Lorillard's *Newport* passed Brown & Williamson's *Kool* brands in 1991. Within the last few months, *Newport* has passed *Salem* in market share to become the top selling menthol brand.

The menthol cigarette of today owes its origins to Spud Hughes and Colonel Axton, but has changed significantly in response to the changes of the public needs over the intervening years. Modern mentholated cigarettes are formulated with the menthol smoker in mind. Advertising has changed accordingly to reflect the changes in lifestyle and to appeal to the current wants of the menthol cigarette smoking public. Advances in the understanding of tobacco in the areas of cigarette construction, blending, and flavor applications, along with visually appealing advertisements, allow today's tobacco companies to meet the wants of increasingly selective and discriminating menthol cigarette smoking customers.

SUMMARY

In the late 1920's, *Spud* became a reality. In the 1930's, the early entries were first *Penguin* and then *Kool*. In the 1940's, the market was small but consistent at about 2%. In the 1950's, the filters were introduced, *Salem* leaped into the lead, and methol was accepted and grew. In the 1960's, the growth continued and some new brands came and went. In the 1970's, the growth topped out at about 30% and more brands were introduced. In the 1980's, the menthol percentage dropped slightly to 26% and the brands proliferated. In the 1990's, opportunity exists for better design and formulation.

FIG. 2

Percent Of Market Share For Menthol Cigarettes

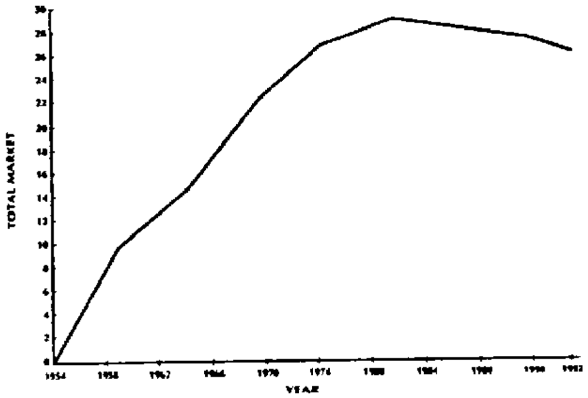


FIG. 3
Menthol Brands Introduced

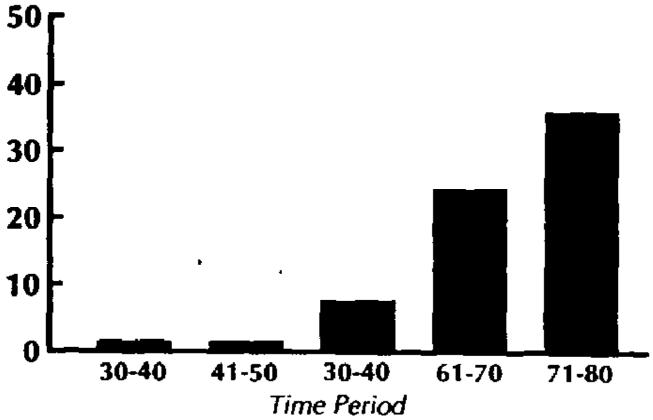
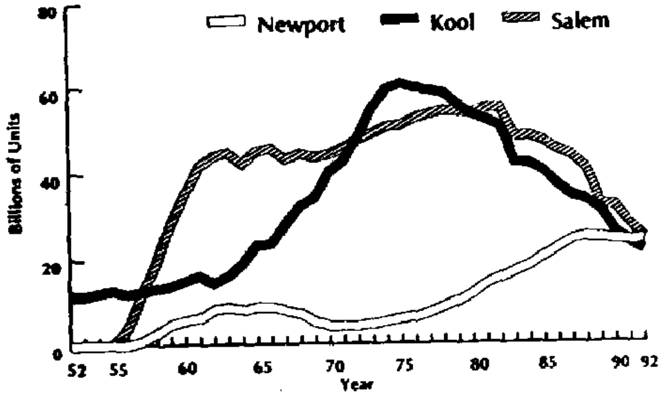


FIG. 4
Leading Menthol Brands
1952 - 1992



ACKNOWLEDGEMENTS

I would like to acknowledge the assistance of Dr. Tom Perfetti at R. J. Reynolds as well as that of Don Redmond, Jeff Kuhl, and Keith Worrell of the Lorillard Audio Visual Communications Section, for the slide preparation. I especially wish to thank Gennie Greene, Starr Pennington and Maria Miller, of the Lorillard Library staff, for the basic research needed to accumulate this information. I also wish to thank Mr. Joe Hudgins, whose private cigarette pack collection was invaluable for slide preparation and Mr. A. Dale Coates, Historic Site Manager of the Duke Homestead State Historic Site, for valuable information.

REFERENCES

1. Corina, M. 1975. Trust in Tobacco: The Anglo-American Struggle for Power. Michael Joseph Publishing, London, p 237.
2. Heinmann, R. K. 1960. Tobacco and Americans. McGraw-Hill Book Company, New York, p 255.
3. Hughes, Lloyd F. September 25, 1925. U. S. Patent No. 1,555,580.
4. Mullen, C. 1979. Cigarette Pack Art. St. Martin's Press, New York, pp 92-94, 105.
5. Nicholls, W. H. 1951. Price Politics in the Cigarette Industry. The Vanderbilt University Press, Nashville, Tennessee.
6. Sabel, R. 1978. They Satisfy - The Cigarette in American Life. Anchor Books/Doubleday, New York, New York, p 108.
7. Anonymous. 1932. Spuds. *Fortune*. 6:51.
8. TJI Report. 1984. The situation on the world menthol market. *Tobacco Journal International*. (5):404-405.
9. Whitten, I. T. June, 1979. Brand Performance in the Cigarette Industry and the Advantage of Early Entry, 1913-74. Federal Trade Commission, Bureau of Economics, Washington, D. C., pp 28-31.

47th Tobacco Chemists' Research Conference

THE CHEMICAL DETERMINATION OF MENTHOL IN THE TOBACCO INDUSTRY FROM AN HISTORICAL PERSPECTIVE

Michael F. Borgerding

R. J. Reynolds Tobacco Company
Bowman Gray Technical Center
P. O. Box 1487
Winston-Salem, NC 27102

ABSTRACT

A general overview of the apparatus, procedures and instrumentation applied to the determination of menthol as it relates to the tobacco industry is presented. Evolution and refinement of chemical analyses for the determination of menthol in tobacco, cigarette smoke, cigarette components and flavoring materials are reviewed. Particular emphasis is placed on summarizing and comparing reported method validation data.

PROLOGUE

As I began to think about this symposium paper, I considered some of the most boring research papers I had ever read or listened to. As I recalled those papers, I realized that the experimental section of a boring research paper can make the rest of the paper look pretty exciting. A paper on analytical methodology has the potential to be a lot of experimental sections strung together. Not to worry. About this time I remembered "PIN"--an acronym for the ideal way to consider new thoughts, ideas and, yes, even manuscripts (62). When applying "PIN", first consider the Positive, next the Interesting and then the Negative.

From the positive side, there have been many interesting analytical methods developed and applied to the determination of menthol. On reviewing the menthol literature my interest peaked. Each paper added to an overall story. As you read this review, my hope is that the original negative thoughts that I had will not surface in you......enjoy.

INTRODUCTION

Since the introduction of the first mentholated cigarette (2, 32), an assortment of chemical analyses have been applied to meet the diverse demands for menthol analysis within the tobacco industry. Chemical analyses have been developed to track or address: (a) the application of menthol to tobacco during cigarette manufacturing, (b) migration and equilibration of menthol within the cigarette and cigarette pack, (c) the fate of menthol upon smoking, with special emphasis on the menthol yield to mainstream smoke, and (d) the purity of menthol and the chemical composition of menthol containing flavors.

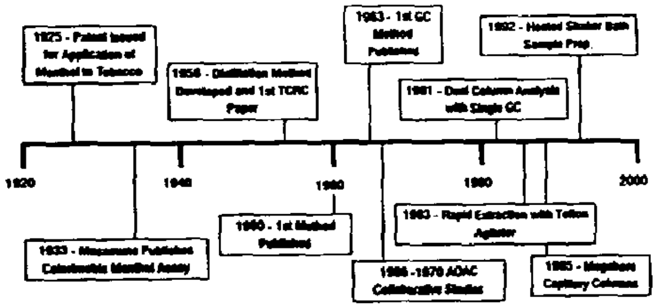
This paper will consider analytical methods developed in several of these areas. Emphasis will be placed on (a) the historical aspects and evolution of current menthol analysis technology, and (b) the figures of merit which have been reported to describe a particular method, i.e., method accuracy, precision, selectivity, and limit of detection.

THE DETERMINATION OF TOBACCO MENTHOL

With the advent of mentholated cigarettes in 1925 (2, 32), chemists were faced with the development of analytical methodology to monitor the application of menthol on tobacco. A simple chronology denoting significant events in the evolution of this measurement is presented in Figure 1. This time line is intended to emphasize the diversity in analytical approach which has evolved since the introduction of mentholated cigarettes, as well as the creativity of the many scientists who have contributed to this field.

FIG. 1

Tobacco Menthol Analysis Time Line



The events from 1925 to present can be separated into three distinct periods, each with a different principle focus. From 1925 to 1963, research efforts were directed to the identification and development of a selective analysis approach which was specific for menthol. The bulk of the work during this period occurred after the introduction of the first successful filtered menthol cigarette brand in 1955. From 1966 to 1980, research emphasis shifted to refinement of analysis accuracy and precision. Finally, having developed several suitable tobacco menthol methods, research from 1981 to present has been concentrated on ways to increase sample throughput, while maintaining accuracy and precision.

EARLY APPROACHES TO SELECTIVE TOBACCO MENTHOL DETERMINATION

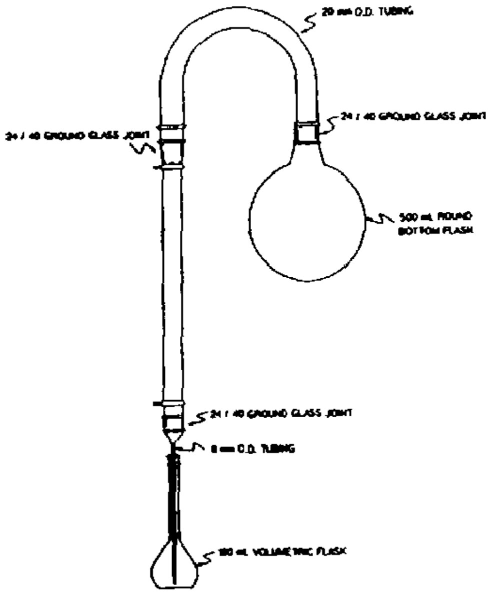
The selective determination of menthol was difficult prior to the mid 1950's. Early analysis methods relied on optical rotation for the determination of tobacco menthol content. For example, in one such procedure tobacco was steam distilled and menthol was extracted from the aqueous distillate with chloroform (27). The rotation of the chloroform solution was then determined. Both the sensitivity and selectivity of this method were limited. Large sample sizes and small solvent volumes were necessary to yield a detectable rotation, with some rotation attributable to sources other than menthol. Obsolescence of this approach was to come, circa 1956, as several scientists took note of earlier work by Masamune (45).

In 1933, Masamune reported a colorimetric procedure for the determination of menthol in tissue and blood. In the procedure, protein was removed by ethanol extraction and filtration. The extract was then distilled at 70°C and the menthol content determined with p-dimethylaminobenzaldehyde in the presence of sulfuric acid by monitoring the red color produced. Adaptations of Masamune's procedure were to form the basis for tobacco menthol determination throughout much of the tobacco industry for many years, and even today menthol analysis with a colorimetric end-determination is still practiced.

In 1956, T. Gibson Harrell completed the development and validation of a new, selective method for menthol on tobacco (27). The method separated menthol from tobacco by distillation, providing a relatively "clean" extract compatible with a colorimetric end-determination according to chemistry adapted from Masamune. The fact that menthol could be separated from tobacco by distillation rather than by direct solvent extraction was a key finding in this work. Unfortunately, solvent extracts of tobacco contained many compounds that could react within the bounds of the chemistry described by Masamune. Tobacco samples with or without menthol were found to develop unacceptable color when extracted with ethanol, carbon tetrachloride, hexane, chloroform, acetone or ether. As colorimetric end-determination for tobacco menthol was considered by other workers, significant diversity was demonstrated in dealing with this limiting phenomenon (15, 42).

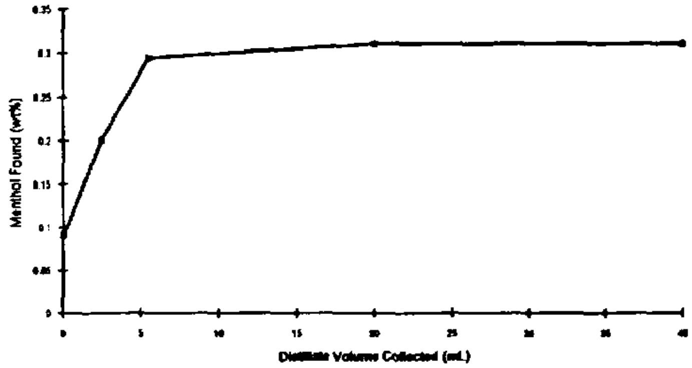
One of the most impressive aspects of Harrell's work is the method validation rigor which he applied. Method precision and accuracy were carefully characterized. Distillation was accomplished with the apparatus shown in Figure 2 without the addition of steam; a gentle flame provided sufficient heat.

FIG. 2
Distillation Apparatus Of Harrell (27)



Twenty milliliters of distillate were required for maximum menthol recovery (Figure 3), hence sample preparation was relatively rapid.

FIG. 3
Distillate Volume Required For Quantitative Measurement



To ensure end-determination accuracy as applied to a mentholated tobacco distillate, the heating time for maximum color development and the temporal stability of the colored-complex formed were characterized. It was found that a two minute heating time (Figure 4) yielded maximum color which was stable for approximately 15 minutes (Figure 5). Based on the transient nature of the colored-complex, it was recommended that absorbance measurements be made as rapidly as possible after the color was fully developed.

FIG. 4
Influence Of Heating Time On Absorbance

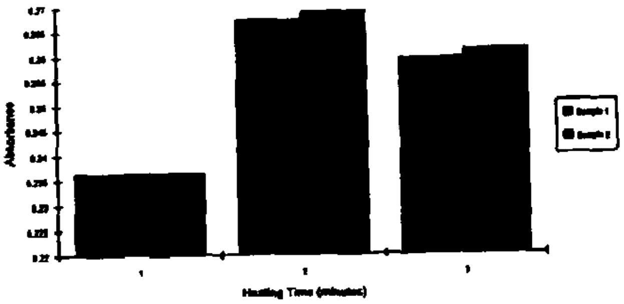
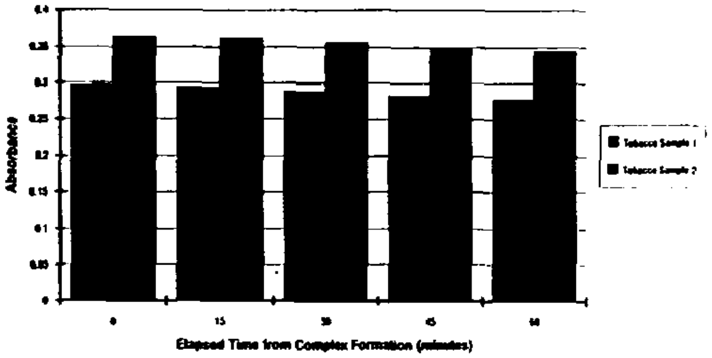


FIG. 5
Stability Of Colored-Complex At Room Temperature



After establishing suitable distillation and end-determination parameters, overall method accuracy was assessed by a recovery study. Known quantities of menthol were added to tobacco and menthol determinations were made (Table I). The average recovery observed was 99.8%.

TABLE I

Colorimetric Method Recovery Study

Menthol Added (mg)	Menthol Found (mg)	Recovery (%)
5.11	5.07	99.3
5.11	5.13	100.3
5.11	5.08	99.5
1.560	1.558	99.8
10.22	10.22	100.0
	Average Recovery	99.8

Method precision was estimated by performing duplicate determinations on a number of cut filler tobacco samples. Average method precision was found to be ± 1% (Table II).

Sample-to-sample variation for typical mentholated cut filler tobacco was found to be approximately 7% to 8%.

TABLE II

Estimation Of Method Precision

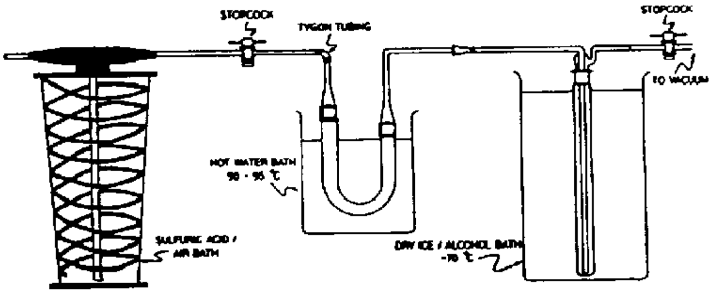
Determination #1 (Weight %)	Determination #2 (Weight %)	Relative Variation (%)
0.302	0.310	1.8
0.253	0.256	0.8
0.262	0.260	0.5
0.257	0.258	0.3
0.256	0.257	0.3
0.280	0.286	1.5
0.311	0.308	0.7
0.285	0.287	0.5
0.263	0.262	0.3
0.291	0.300	2.2
0.286	0.282	1.0
0.263	0.276	3.4
0.310	0.309	0.2
	Average Precision	± 1.0

The attention to detail in the development and validation of this analysis produced one of the most desirable attributes for an analytical method--longevity. It is interesting to note that this method was later chosen as one of two unpublished methods for collaborative study under the auspices of the Association of Official Analytical Chemists (AOAC) (1, 55, 56, 64, 65, 66) and it is currently an official AOAC method for the determination of tobacco menthol (55).

Several other approaches to the determination of menthol via colorimetric end-determination have been reported. Each method addressed, in a unique way, the critical problem of separating menthol from tobacco while providing for selective detection of menthol without interference from other tobacco constituents. At this conference in 1956, R. D. Carpenter and R. B. Seligman of Philip Morris reported a method which used drop-wise extraction of a single cigarette (15). According to their procedure, an aliquot of the ethanol extract was aerated with nitrogen for one hour. In this manner, menthol was selectively separated and collected for determination by reaction with p-dimethylaminobenzaldehyde.

J. J. Lubus and H. D. Bogue of P. Lorillard Company advocated solvent extraction followed by distillation to solve the selectivity problem in the first published procedure for the determination of menthol in mentholated cigarettes (42). Using the apparatus shown in Figure 6, an ethanol extract of mentholated tobacco was distilled with an air stream which was first drawn through a sulfuric acid bath. Menthol was then determined colorimetrically after reaction with p-dimethylaminobenzaldehyde.

FIG. 6
Distillation Apparatus Of Lubus And Bogue (42)



Several details from this procedure are important to consider. First, the sample size and extraction volume reported were six cigarettes and 150 ml, respectively. This is a larger sample size than was used by either Carpenter and Seligman (one cigarette) or Harrell (2 grams). Second, an extraction time of two hours while continuously shaking at room temperature was recommended for quantitative results. This particular method parameter has been extensively studied in the years that have followed. Accurate, precise recovery of known amounts of menthol added to tobacco was found with these conditions (Table III).

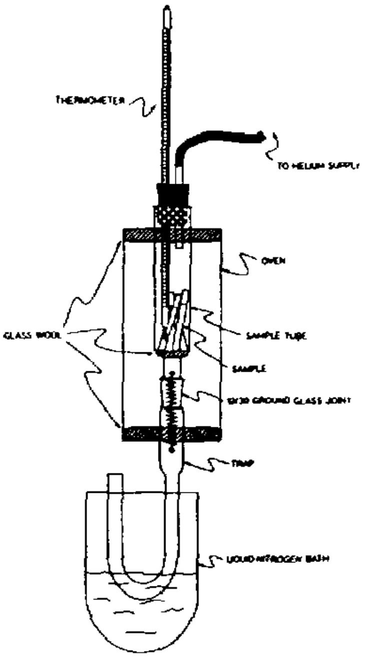
TABLE III

Recovery Study According To The Method Of Lubus And Bogue

Menthol Added (mg/ml)	Menthol Found (mg/ml)	Menthol Found (mg/ml)	Menthol Found (mg/ml)	Average Recovery (%)
0.035	0.036	0.036	0.034	101
0.050	0.051	0.050	0.050	101
0.075	0.076	0.075	0.073	100
0.085	0.091	0.084	0.091	104
0.100	0.104	0.101	0.100	102
0.125	0.125	0.125	0.124	100
Recovery Grand Average				101

In addition to rock music, hippies and anti-war demonstrations, the 1960's brought something useful for analytical chemistry--gas chromatography began to emerge as a valuable analysis tool. Betty Mitchell et al. from the American Tobacco Company published the first method for the chromatographic determination of menthol in cigarettes and cigarette smoke (48). The method involved the vaporization of menthol in a helium stream, with subsequent collection in a liquid nitrogen cooled U-trap (Figure 7). Menthol collected in the cryogenic trap was dissolved in chloroform and analyzed by gas chromatography with a Carbowax 550 stationary phase. The method was found to be both accurate (96% to 102% recovery) and precise.

FIG. 7
Vaporization And Collection Apparatus Of
Mitchell, Barbee And Irby (48)



As a chromatographer by training, I found this work both interesting and enjoyable. It is interesting that the technique described is analogous in some aspects to both static and dynamic headspace GC. Despite the commercial availability of this instrumentation, headspace GC methods have not been reported to date for the determination of menthol on tobacco. Reflection on the instrumental analysis conditions described in the work brought a smile to my face. Injection volumes of 25 µl, column flow rates of 150 ml per minute and manual injection (!) are conditions which many of today's analysts have never seen. Yet with all of the refinements to chromatographic analysis in the last thirty years, the principal differences realized for menthol analysis from 1963 to 1993 are not accuracy and precision, but rather sample throughput and operator ease of use.

REFINEMENT OF METHOD ACCURACY AND PRECISION

With the development of chromatographic methods, tobacco chemists had two different techniques available to determine menthol on tobacco, colorimetric and chromatographic. The primary analytical challenge, i.e., selective chemical determination, had been largely solved. The continuation of work in this area began to focus on the refinement of method accuracy and precision.

The validation of method accuracy is frequently the most difficult part of any method validation process. Currently, accepted procedures for assessing method accuracy include: (a) analysis of certified reference materials, (b) comparison to standard reference methods, (c) use of standard addition/ recovery techniques, (d) comparison of results over a range of method conditions with a single method, and (e) comparison to other working methods, i.e., other methods not accepted as official reference methods.

Although the first two approaches are preferred, these were not possible with early tobacco menthol methods. The third and fourth methods, use of standard addition/recovery techniques and comparison of results over a range of method conditions, were applied to validate method accuracy during the late 1950's and early 1960's. However, with multiple analysis techniques available, the last approach, comparison of different working methods, was also applied to validate method accuracy in a series of AOAC collaborative studies conducted from 1966 to 1970 (1, 64, 65, 66).

Two AOAC collaborative studies were conducted which each compared a colorimetric method and a gas chromatography method, leading to the adoption of both of these methods as official AOAC methods in 1970 (55, 56). It is interesting to note that both methods evaluated in these studies were previously unpublished. The colorimetric procedure was the method of Harrell, which has been described in detail, and the gas chromatography method was the method of Wickham and Bennett of Philip Morris. In the latter method, mentholated tobacco was extracted with ethanol and the extract was analyzed by gas chromatography without further clean-up.

The first collaborative study, published in 1967 by C. L. Tucker of P. Lorillard Company, involved fifteen collaborators, fourteen of whom applied both methods to three different mentholated tobacco samples (65). Quadruplicate determinations of each tobacco sample were completed by each method. Solvent extraction in the GC method consisted of mechanical shaking for one hour followed by passive extraction overnight. Findings reported from this work included: (a) no significant differences were observed between means with the two methods for any sample, although a trend to higher mean values with the colorimetric method was noted and (b) no statistically significant differences within or between laboratories were found, although a trend to lower within-laboratory standard deviations with the gas chromatographic method was also noted.

A second collaborative study was completed and published in 1968 (66). This study was designed to determine if the tendency to slightly greater colorimetric values in the first study was due to the choice of "blank" correction. Both a reagent blank and a nonmentholated tobacco blank were included as part of the colorimetric determination in the study design. The gas chromatography method was also modified slightly. The sample extraction time was shortened to two hours of mechanical shaking. Thirteen collaborators participated in the second study, with twelve applying both methods.

Results from the second study were virtually identical to the first study. Use of a nonmentholated tobacco blank seemed to reduce the perceived difference in mean values obtained with the two methods. Hence, both the nonmentholated tobacco blank and the two hour ethanol extraction time were adopted in the final, official methods.

It is interesting, perhaps even a statement to the analytical chemists' mentality, that a relatively small difference in mean values for the two methods--a difference stated as insignificant in both reports--should be the object of such consideration and attention. Figure 8 and Figure 9 present the observed differences between methods for one sample from each study. Differences are plotted as colorimetric result minus GC result for each collaborator.

FIG. 8
Difference Comparison Of First AOAC
Collaborative Study Sample #1

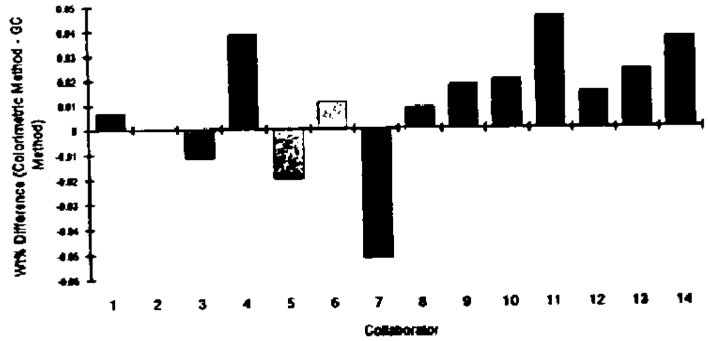
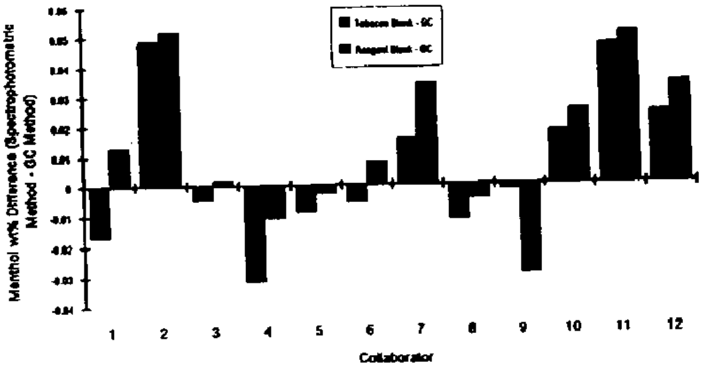


FIG. 9
Difference Comparison Of Second AOAC
Collaborative Study Sample #3



Examination of these figures which are somewhat akin to residual plots used in statistical analyses reveals: (a) there is no consistent directional bias--both positive and negative difference results are found in both studies, although the differences are weighted to greater colorimetric method response, (b) both negative and positive values are obtained for the difference regardless of which blank correction technique is used for the colorimetric method, and (c) the absolute magnitude of the observed response is roughly ± 0.05% by weight of menthol on tobacco.

It is important to note that consideration was given in both collaborative studies to the premise that the colorimetric procedure may have yielded (marginally) inflated results, but no data are available which independently verify that the extraction procedure yields quantitative data. Review of the various sample preparation procedures and conditions which have been reported to yield quantitative analysis (Table IV) confirms that (a) menthol addition to samples and (b) "maximum response" optimization have each been used to establish menthol recovery; i.e., sample preparation accuracy. Experiments in which menthol is added to the sample invariably yield rapid and largely quantitative results under a wide range of analysis conditions. The limited number of experiments in which extraction time is studied to determine maximum response suggest that quantitative menthol extraction may not be achieved quickly. Based on this point of difference, further consideration of the two techniques is warranted.

The former technique involves the addition of known amounts of menthol to representative tobacco samples, analysis of the sample and comparison of the amount found with the amount added. It is not always clear from the literature exactly how the menthol is added, or to what it is added in the experiments that have been reported. In some cases, menthol is added to tobacco and the sample is permitted to "dry" or equilibrate. In others, it appears that menthol may have been added to the tobacco in the extraction solvent.

TABLE IV

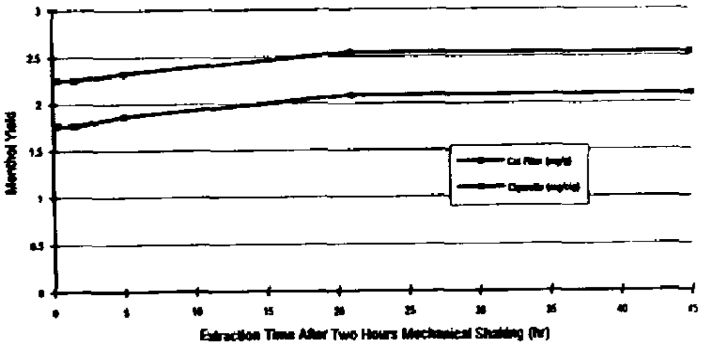
Summary Of Sample Preparation Procedures, Recovery Data And End-Determinations Reported For The Determination Of Tobacco Menthol

Study	Preparation Technique	Stated Recovery (%)	Technique Used To Determine Recovery	End-Determ.
Harrell, 1956 (27)	Distillation	99.8	Maximum Response, Menthol Addition	Color.
Lubus and Bogue, 1960 (42)	Ethanol Extraction (2 Hrs) Followed By Distillation	101	Menthol Addition	Color.
Nesemann and Seehofer, 1972 (52)	Distillation	97	?	GC
Brozinski et al., 1972 (13)	Distillation	98.4 (86 To 103)	Menthol Addition	GC
Yasumatsu et al., 1977 (69)	Ethanol Extraction (2 Hrs Mechanical Shaker + ~20 Hours Passive)	99 To 100	Maximum Response	GC
Curran, 1972 (18)	Methanol Extraction (1 Hr)	101.2	Menthol Addition	GC
Curran, 1975 (19)	Ethanol Extraction (2 Hrs)	Not Reported	---	GC
Frank, 1983 (22)	Methanol Extraction (15 Min/Special Shaker)	99.6	Menthol Addition	GC
Hicks and Dunlap, 1993 (31)	Ethanol Extraction (1 Hr Mechanical Shaker + ~23 Hours Passive)	99 To 100	Maximum Response	GC
Hicks and Dunlap, 1993 (31)	Ethanol Extraction (Heated Shaker Bath, 50 Minutes)	100	Maximum Response	GC

In any event, the fundamental problem when adding a material for the purpose of testing analysis recovery is verification that a chemical matrix has been produced which is analogous to and representative of the actual test sample of interest. In essence, the addition of a standard material "models" the sample matrix, with the quality of the recovery estimate dependent upon the quality of the model. This potential limitation is not unique to the determination of tobacco menthol and it does not invalidate the approach, *a priori*. However, it must be considered with regard to ultimate method validity.

Some authors establish quantitative sample recovery by maximizing the analyte *response* across all pertinent analysis variables. For example, menthol response might be determined as a function of sample extraction time to define the length of time required before a maximum and consistent response is observed. Figure 10 is such an experiment from work by Yasamatsu *et al.* (69). Menthol respónse was determined at various times during an extended passive extraction period which followed an initial, two-hour period of mechanical shaker extraction.

FIG. 10
Effect Of Additional Passive Extraction After
Two Hours Of Mechanical Shaking With Ethanol



It is clear from this figure that a maximum and consistent response was not observed in Yasamatsu's work until approximately twenty hours after mechanical shaking was completed. While this approach has the advantage of defining a functional relationship between analyte response and analysis parameters, in the strictest sense, optimized maximum response alone does not ensure quantitative recovery and response.

Ideally, it is desirable that both experiments, recovery of added standards and maximum response, be conducted for the purposes of method validation. Clearly, if consistent results are not obtained by the two methods, then further experimentation is needed.

It is the opinion of this author that the conclusion detailed by Tucker in the second AOAC collaborative study (66) is correct--either method is suitable for the determination of tobacco menthol. Why then, have the last several pages of this manuscript focused on (some might suggest "quibbled about") the small reported differences between the two official AOAC methods. Academic interest and the pursuit of absolute accuracy play a part, of course. The most compelling reason is practical, however. Tobacco menthol method accuracy affects conclusions which may be drawn from menthol migration studies. The ability to accurately detect small changes in tobacco menthol content is not particularly significant to the production of mentholated tobacco, but it is critical to determining precisely when migration within a cigarette has reached a steady state and equilibration has been achieved.

WAYS TO INCREASE SAMPLE THROUGHPUT AND IMPROVE TOBACCO MENTHOL ANALYSIS EFFICIENCY

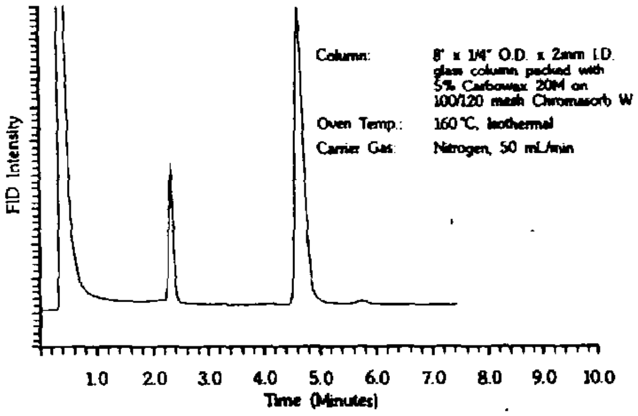
With the ever increasing popularity of mentholated cigarettes from 1960 to 1985, the need for improved sample throughput when determining tobacco menthol has been paramount. Tobacco or whole cigarette menthol is often used as a quality assurance end point for the production of mentholated cigarettes, hence sample throughput requirements may number in the hundreds of samples per day. Gains in sample throughput have been achieved by the development of methods which yield: (a) shorter end-determinations, (b) more end-determinations per instrument per unit time, (c) shorter sample preparation times, and (d) multiple analytes per analysis.

Reported studies have tried not only to achieve maximum sample throughput, but also to minimize apparatus and instrumentation cost. Thus, efficiency, rather than a "brute force" approach, has been an analysis goal.

With my co-author, Bert Gordon, I presented the use of dual, simultaneous chromatographic analyses in a single GC oven at this conference in 1981 as a means of increasing sample throughput (26). Commercially available instrumentation coupled with "fast GC columns" enabled approximately 40 samples per hour per instrument to be completed. Later studies in our laboratories suggested that the packed columns reported were not suitable for all commercially available menthol cigarettes. Therefore, based on subsequent work, we adopted a packed column with a Carbowax stationary phase (Figure 11) (8). A throughput of ~20 samples per hour per instrument is possible with this column in a dual analysis configuration, largely due to the chemical simplicity of the distillate sample. With few peaks to separate--propylene glycol, nicotine, glycerol and neophytadiene although prevalent when samples are extracted are largely absent in the distillate--short chromatographic run times are possible.

Other workers have reported ways to reduce sample preparation time in order to increase throughput. M. S. Frank of Brown & Williamson reported the use of a novel extraction technique at the 37th TCRC which substantially reduces preparation time by pulverizing the sample during extraction (22). In the procedure, a Teflon agitator is present in each sample and samples are agitated at 650 to 700 rpm, yielding quantitative extraction in 15 minutes. R. D. Hicks and S. P. Dunlap of R. J. Reynolds Tobacco Company have developed a method based on extraction in a heated shaker bath (31). Quantitative extraction with ethanol is possible in about an hour (Figure 12).

FIG. 11
Typical Packed Column Separation Of
Mentholated Tobacco Distillate



Column: 8' x 1/4" O.D. x 2mm I.D. glass column packed with 5% Carbowax 20M on 100/120 mesh Chromasorb W

Oven Temp.: 160 °C, Isothermal

Carrier Gas: Nitrogen, 50 mL/min

FIG. 12
Menthol Response As A Function Of
Heated Shaker Bath Extraction Time

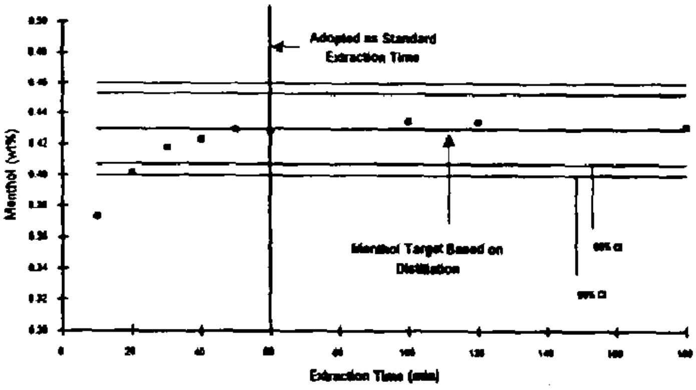


Table V attempts to summarize and compare the relative throughput of various methods which use gas chromatography for the end-determination. Based on use in the literature (22), throughput is defined for the purposes of this table as the number of samples which can be analyzed from start to finish by one analyst with one gas chromatograph during a single eight hour shift.

Another approach to maximizing the sample "cost/benefit" ratio is to target multiple analytes per analysis. Including multiple analytes in a single analysis provides an efficient way to minimize cost and maximize total sample throughput. It is not necessarily the fastest way to process a group of samples if menthol is the only analyte of interest. At the 41st TCRC, M. S. Frank and O. C. Lin of Brown & Williamson Tobacco Corporation reported an adaptation of Frank's earlier menthol work, combining humectant, plasticizer and menthol methods into a single analysis (23). Multiple analytes were separated in about 8 minutes with a J&W DB-WAX Megabore capillary column. Sample throughput for a single analyst with one chromatograph is estimated to be about 40 samples per eight hour shift.

ANALYSIS PRECISION CONSIDERATIONS WHEN DETERMINING TOBACCO MENTHOL

Analysis variation or "measurement error" is inherent in all chemical determinations. The overall variance for a particular method is the sum of individual variance components. For the determination of menthol on tobacco, predominant contributions to the total method variance include: end-determination variance, sample preparation variance, product sampling variance and manufacturing variance. Recent experiments conducted in our laboratory provide a crude estimate of the relative contributions to the total variance from each of these sources (7).

TABLE V

Sample Throughput Summary For Methods Which Use Gas Chromatography As The End-Determination

Method	Sample Preparation Time (min)	Samples Prepared Per Run	Approximate GC Run Time (min)	Throughput
Room Temperature Extraction (56)	120	24	10	36
Distillation (26)	20	40	5	120
Heated Extraction (31)	60	20	7	75+
Pulverized Extraction (22)	20 To 35	20	5	75+

Notes:
(1) All throughput values assume instrument calibration occurs during first sample preparation period.
(2) A dual column instrument configuration and a 1.5 minute autosampler injection sequence time were considered for throughput calculations with the second and third procedures.
(3) A mechanical shaker with 24 sample capacity was assumed for first procedure.
(4) The sample preparation time for last procedure includes a 15 minute extraction time and a 5 to 15 minute settling time.

In the experiments, GC end-determination variance was estimated during a two week period by repetitive sample injection on each day of the study (Experiment #1). Sample preparation variance was established by analyzing replicate samples per pack of mentholated cigarettes on each day of the study (Experiment #2). Combined product sampling and manufacturing variance was approximated from long-term analysis results during a multimonth period (Experiment #3). Thus, these three experiments together provide a means of separating individual variance contributions when treated as a series of simultaneous equations.

$$\sigma^2_{Exp.\,1} = \sigma^2_{End\ Determ.}$$

$$\sigma^2_{Exp.\,2} = \sigma^2_{Sample\ Prep.} + \sigma^2_{End\ Determ.}$$

$$\sigma^2_{Exp.\,3} = \sigma^2_{Product\ Sampling\ /\ Manufac.} + \sigma^2_{Samp.\ Prep.} + \sigma^2_{End\ Determ.}$$

Figure 13 illustrates the apportionment of total method variance among the significant sources for three different mentholated brand styles: a full flavor (FF) brand, a full flavor low 'tar' (FFLT) brand and an ultra low 'tar' (ULT) brand. For FF and FFLT brand styles, product sampling/manufacturing variation is the largest variance component, with sample preparation and end-determination contributions ranking second and third in order of significance. The observed relationship between the variance components with these brand styles is typical of what has been reported in the literature for other analytes (68).

For the ULT brand style, sample preparation was found to account for ~87% of the total method variance (Figure 13). Assignment of this large proportion is artifactual, however. Implicit in the experimental design used, is the assumption that the cigarettes within each pack studied were completely homogeneous. For the ULT brand studied, significant variation existed throughout each pack of cigarettes (Figure 14), hence sample preparation and product sampling/manufacturing variation could not be effectively separated. It is interesting that the total variance observed for the ULT brand studied was an order of magnitude greater in absolute terms than that of either the FFLT or FF brand styles.

FIG. 13
Apportionment Of Variance Contributions For Tobacco Menthol Determination

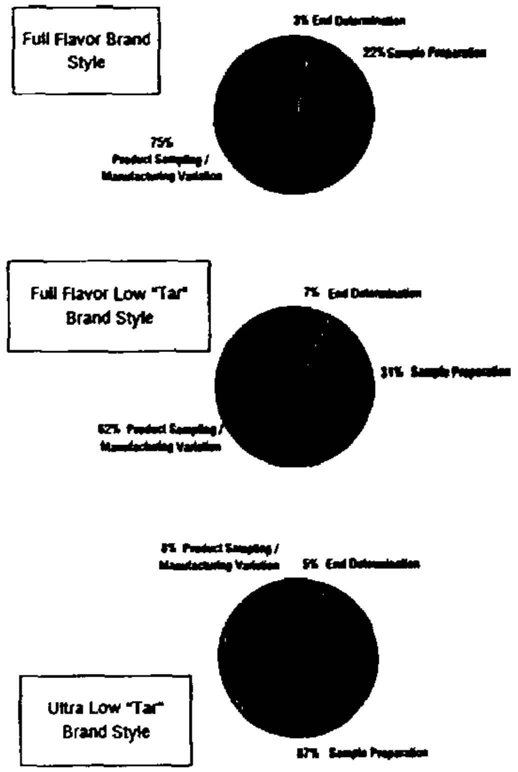
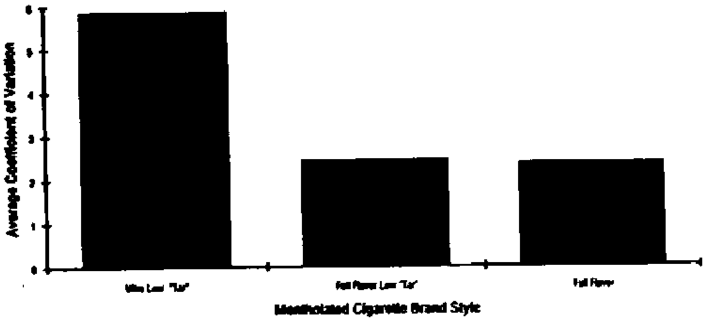


FIG. 14
Menthol Variation Within The Cigarette Pack
On The First Days After Manufacturing

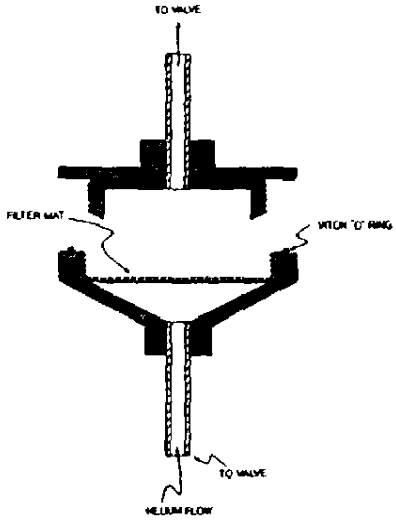


THE DETERMINATION OF MENTHOL IN SMOKE

The successful determination of menthol in mainstream cigarette smoke lagged some years behind that of menthol in tobacco. Technical challenges related to the chemical complexity of smoke were a primary reason for the slower pace. The fact that smoke menthol is not a typical manufacturing endpoint probably contributed as well. Smoke menthol studies have generally consisted of either the determination of menthol in mainstream smoke to assess the effects of some fabrication or aging parameter on menthol yield, or more specialized materials balance studies to determine the complete fate of menthol upon smoking. Each analysis type will be considered in turn.

Early attempts to determine menthol in smoke with tobacco methods proved largely unsuccessful because of interferences from other smoke components (27, 42, 43). Mitchell et *al.* in 1963 (48) and Lyerly in 1967 (43) capitalized on menthol volatility to overcome this limitation. In both methods, menthol was selectively eluted from mainstream smoke collected on Cambridge filters by passing a helium stream through the filter while heating. Menthol was thus volatilized from the Cambridge filter, while the less volatile smoke components were retained. The two methods differed in one key feature. The method of Mitchell *et al.* collected the volatilized menthol in a cold trap for subsequent GC analysis (Figure 7), while in Lyerly's method, menthol vapor was transferred directly to the GC column from the apparatus in Figure 15. One advantage of the latter approach was increased sensitivity, enabling puff-by-puff menthol data to be generated.

FIG. 15
Special Cambridge Filter Holder
From The Method Of Lyerly (43)



Brozinski and co-workers found that, as with tobacco, smoke could be steam distilled, partitioned into methylene chloride and analyzed by gas chromatography (13). Their work stands out from most reports, in that a complete set of method validation data is reported. Method precision (CV) was found to be 4%, recovery through the sample preparation procedure was found to be 100.2%, and the trapping efficiency of Cambridge filters (CF) and electrostatic precipitation (EP) for smoke menthol was compared.

Brozinski *et al*. found that some menthol passed through the EP smoke trap and condensed in a second trap containing glass wool impregnated with triacetin. In addition to breakthrough out of the EP trap, the total amount of menthol found in the EP and the second trap was less than that found with the CF trap (see Table VI).

TABLE VI

Comparison Of Smoke Menthol Collection By EP And CF

	Smoking #1	Smoking #2	Average
Cambridge Filter/Filtrona CSM 10 Smoking Machine			
Cigarettes Smoked	5	5	Average
Menthol In Main Trap	0.44	0.47	0.46
Menthol In Second Trap	0.00	0.00	0.00
Total Menthol	0.44	0.47	0.46
Electrostatic Precipitation/Borgwaldt RM 20/68			
Cigarettes Smoked	20	20	Average
Menthol In Main Trap	0.39	0.42	0.41
Menthol In Second Trap	0.02	0.02	0.02
Total Menthol	0.41	0.44	0.43
Note: All menthol values are mg/cig. The second trap consisted of glass wool impregnated with triacetin.			

Electrostatic precipitation has been used extensively in my laboratory, this technique often being the preferred smoke collection method in our work (10, 11). Subsequent sample preparation of neat total particulate matter (TPM) collected by EP is often simple. Based on a scientific fondness for EP collection, the earlier work of Brozinski was recently repeated and expanded in our laboratory (9). The two smoke collection techniques were compared by replicate smokings with three different mentholated brand styles. Results in Table VII show good general agreement between EP and CF smoke menthol collection.

It should be noted that in addition to the main EP trap, two cryogenic solvent traps containing methanol, the first maintained at 0°C and the second at -70°C, were placed after the EP trap in this experiment to determine if menthol collection was less than quantitative (Figure 16). Measurable amounts of menthol (0.01 mg/cigarette or greater) were not detected in either trap for any brand style. These data suggest, therefore, that EP is a suitable smoke menthol collection technique. Differences in the results of the two studies were due, possibly, to refinements in EP trap design over the years.

TABLE VII

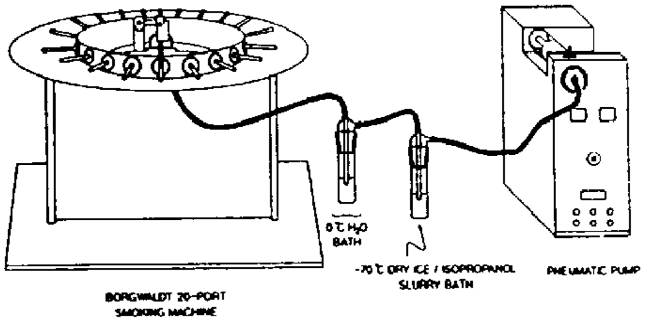
Recent Comparison Of EP And CF Smoke Menthol Collection Efficiency With Three Brand Styles

	ULT Brand	FFLT Brand	FF Brand
Smoke Menthol (mg/cig)			
Electrostatic Precipitation	0.33 ± 0.02	0.60 ± 0.03	0.81 ± 0.04
Cambridge Filter	0.33 ± 0.02	0.57 ± 0.02	0.76 ± 0.02
Mainstream TPM (mg/cig)			
Electrostatic Precipitation	2.8 ± 0.1	13.3 ± 0.5	23.8 ± 1.3
Cambridge Filter	2.5 ± 0.2	13.3 ± 0.5	24.7 ± 1.0

Note: All values are the average ± one standard deviation for six replicate determinations. Twenty cigarettes were smoked for each EP sample and five cigarettes were smoked for each CF sample.

Another unique aspect of Brozinski's work is the fact that data are presented for a smoke menthol trap subsequent to the Cambridge filter. As new cigarette designs are evaluated, it is important to be cognizant that a single Cambridge filter may not collect all smoke menthol. It is conceivable that smoke from new cigarette designs may exit the mouth end at temperatures which differ from most cigarettes sold today. One example of such behavior was the CF menthol trapping efficiency observed for *Premier* cigarettes. With this cigarette, approximately 80% of mainstream smoke menthol was trapped with a single Cambridge filter, while two Cambridge filters yielded quantitative collection (30).

FIG. 16
Electrostatic Precipitation Smoke Collection
With Back-Up Traps



Since the work of Curran reported in 1975 (19), smoke menthol has been determined by collection on a Cambridge filter, direct extraction of the filter and analysis of the extract by gas chromatography. Table VIII summarizes the many extraction solvents and extraction times employed for the measurement of smoke menthol. The diversity of sample preparation conditions found in Table VIII reflects the wide scope of analysis constraints which confront the analyst.

One of the most challenging aspects of determining smoke menthol by gas chromatography is the separation of propylene glycol and menthol. These two smoke components tend to co-elute under many chromatographic conditions. It is possible to separate the two materials, but usually at the expense of a longer analysis time. McMurtrie and Cannon reported a novel approach to this problem in 1979 (46). In their procedure, Cambridge filters are extracted for 30 minutes with a binary mixture of chloroform and water. Propylene glycol partitions into the water layer and is eliminated as a chromatographic interference. Menthol extraction efficiency was reported to be greater than 99% by this procedure with a chromatographic run time of 3 minutes.

TABLE VIII

Conditions Used For the Direct Extraction Of Cambridge Filters When Determining Smoke Menthol

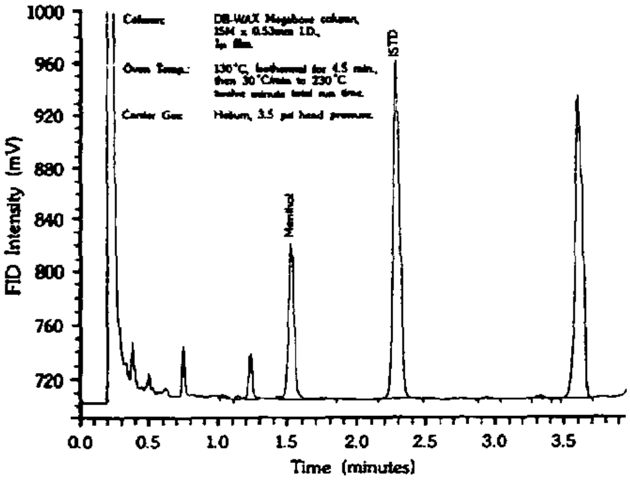
Study	Extraction Solvent	Extraction Time (min)
Curran (19)	Ethanol	120
Yasumatsu (69)	Ethanol	120
McMurtrie and Canon (46)	Chloroform/Water	30
Shoffner and Ireland (61)	Freon 113/ Isopropanol	30
RJR Standard Test Method	Methanol	60
RJR Standard Test Method	Chloroform	Overnight

As with tobacco, some analyses target multiple smoke analytes to maximize overall analysis throughput. As an example, Shoffner and Ireland have reported the use of a trichlorotrifluoroethane/isopropanol binary mixture in a 4:1 ratio for the rapid determination of menthol and nicotine in smoke (61). Average recoveries of menthol and nicotine from the Cambridge filter were reported to be 100%, and equivalent results were found when the method was compared to the official AOAC method for smoke nicotine (57) (menthol was not compared).

It is significant that the literature does not currently include a citation for the use of capillary column GC to determine smoke menthol given the widespread use of capillary GC today. Figure 17 is a typical smoke menthol separation from our laboratory which employs a Megabore capillary column.

FIG. 17

Smoke Menthol Separation With A Megabore GC Column



ANALYSIS OF OTHER TOBACCO SMOKE STREAMS FOR MENTHOL

The chemical determination of menthol in smoke streams other than mainstream smoke has been limited. Sensory evaluation testing of sidestream odor conducted by Gains and Marmor (24) suggests that subjects cannot detect a difference between the sidestream odors of mentholated and nonmentholated cigarettes. In their study, sidestream odor was collected by exposing Cambridge filters moistened with mineral oil to sidestream smoke in a modified bell-jar apparatus. Menthol collection efficiency was not reported.

There have been no reports in the literature which define the collection efficiency of sidestream smoke menthol on a Cambridge filter. It is possible that, like nicotine, menthol is not quantitatively trapped by a Cambridge filter. Cryogenic solvent traps may, therefore, be necessary to study sidestream smoke menthol. Additionally, there may be a dependance upon the type of apparatus used for smoke collection, e.g., a Neurath chamber (53) versus a B.A.T. fishtail chimney (58). Hopefully, this general deficiency in the literature will soon be corrected.

Total smoke collection chambers have been used by a number of workers to determine the fate of carbon-14 labeled menthol in total smoke. In these studies, mainstream smoke TPM, mainstream smoke gasses, sidestream smoke TPM and sidestream smoke gasses are collected and the radioactivity of each sample type determined. Cigarette ash and butt are also assayed for residual radioactivity. An overview of the historical development and refinement of total smoke collection apparatus is beyond the scope of this review. The reader is referred to the literature, therefore, for detailed descriptions of these systems (6, 33, 34, 50, 54, 63).

One finding from radiotracer studies which is pertinent to a discussion of analytical methodology is the amount of radioactivity which is found in the mainstream smoke gasses. Approximately 1% or less of menthol radioactivity has been found in the mainstream gas fraction of smoke. This confirms the fact that mainstream smoke menthol is quantitatively trapped by a Cambridge filter.

ANALYSIS OF MENTHOL AND MENTHOL CONTAINING FLAVORS

Most analyses of neat menthol or menthol containing flavors have historically been conducted to answer one of four questions:

a. What is the quality of the menthol?

b. Is the correct amount of menthol present in tobacco top dressing solutions?

c. Is the correct amount of menthol present in filter flavor solutions?

d. What is the composition of a peppermint or other menthol containing flavor?

Analyses conducted to answer these questions have exploited chemical and physical properties of the menthol molecule. Menthol ($C_{10}H_{20}O$) is a monoterpenoid, secondary alcohol. The chemical structure of menthol contains three asymmetric centers, hence menthol exists in four diasteriomeric forms known as menthol, isomenthol, neomenthol and neoisomenthol. Each diasteriomeric form exists as a racemic mixture. The physical constants for menthol isomers have been well characterized (60). Melting point (M.P.), boiling point (B.P.), specific gravity (d at 15°C), refractive index (n at 20°C) and optical rotation (α) data for some compounds are found in Table IX.

TABLE IX

Summary Of Physical Constants For Menthol Isomers

Compound	M.P. (°C)	B.P. (°C)	d^{15}	n^{20}	$[\alpha]_D^{20}$
(±) Menthol	38	216	0.904	1.4615	---
(-) Menthol	43	216	0.904	1.4609	-49.4
(±) Neomenthol	53	212	0.903	1.4604	---
(+) Neomenthol	-22	212	0.903	1.4603	+19.7
(±) Isomenthol	53.5	219	---	---	---
(+) Isomenthol	82.5	219	---	---	+27.0[2]
(±) Neoisomenthol	14	215	---	1.4649	---
(+) Neoisomenthol	-8	215	0.913[1]	1.4649	+0.14

[1] d^{18}. [2] In alcohol.

Prior to the invention of gas chromatography, menthol was assayed in a number of ways. During the 1930's and 1940's, menthol was determined in peppermint oil based on the presence of the hydroxyl group by acetylation and titration (4, 12, 16, 36, 51). Colorimetric and spectroscopic techniques were also reported (41, 45). Yoshitani *et al.* determined the menthol content of top dressing material colorimetrically and by optical rotation (70). However, the volatility of menthol makes it ideally suited for gas chromatographic analysis (40). Moore and Kossoy reported the separation of menthol isomers on a 12 foot packed column with a Hyprose stationary phase in 1961 (49). Development of gas chromatographic alternatives continued for many years. Gillen and Scanlon published a separation of menthol and menthone isomers using Carbowax 400 in 1972 (25). Haut and Core successfully applied liquid chromatography to the same task, separating all six components in about fifteen minutes (28). The separation of menthol and menthone isomers is relatively straightforward today using capillary gas chromatography, an example of peppermint oil separations can be found in the work of Emberger and Hopp (21). In fact, peppermint oil separations can be found in the applications section of a leading capillary column manufacturers sales catalog (37). Chiral separations of menthol isomers are also possible by either gas or liquid chromatography. The reader is directed to the last two references cited for examples (21, 37).

OTHER ANALYSES

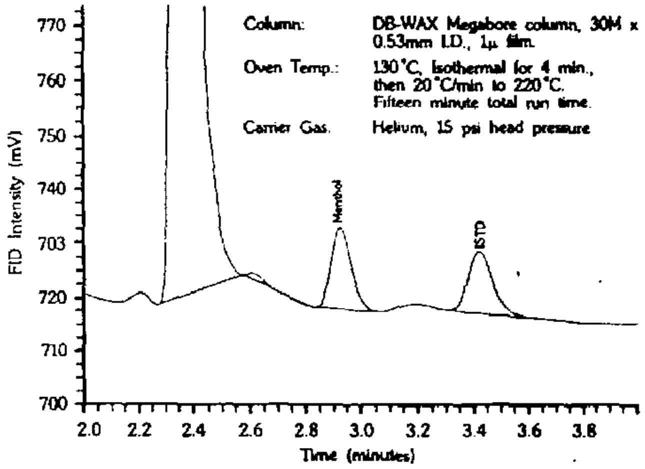
Menthol volatility not only makes the *compound* well suited for GC analysis, but also makes it difficult to keep the compound in a single location within the cigarette pack. Phenomenological data and theoretical aspects of menthol mass transfer and equilibration processes are the subjects of other papers at the symposium. Given sufficient time, menthol equilibrates between the cigarette tobacco rod and filter, as well as the packaging material. As such, chemical analyses for each of these components have been reported.

Tobacco rod analyses have already been described in detail. Most tobacco menthol methods have also been applied to filters (13, 18, 19, 23, 31, 52, 59, 69) and/or the complete cigarette (8, 18, 23, 31, 48, 59). One exception is the filter (only) method of Kaburaki which is based on toluene extraction (38). Considering the collective literature, filter extraction is relatively straightforward, with quantitative menthol recoveries easily achieved (18, 69).

Measurable amounts of menthol have also been found in cigarette packaging materials. Uhrig *et al.* determined menthol in both soft pack and crushproof box materials by methylene chloride extraction followed by capillary GC analysis (67). Mickey evaluated the foil inner wrapper by distillation and gas chromatography (47). More recently, Beard and Hicks have also analyzed packaging by heated shaker bath extraction (5).

Another menthol analysis which the tobacco chemist must consider is the determination of "trace" menthol. Low levels of menthol are of interest both by design and by fate--contamination of nonmentholated tobacco with mentholated tobacco. Most analysts approach "trace" menthol as a maximization problem; the amount of tobacco is increased and the final solvent volume is reduced to increase the final menthol concentration in the sample. Harrall reported measurements as low as 0.025 weight percent menthol when starting with 6 grams of tobacco and 50 ml of distillate (27). Brozinski was able to measure 0.003 weight percent (13) and Hicks easily measures 0.01 weight percent by heated shaker bath extraction (Figure 18).

FIG. 18
Trace Tobacco Menthol Separation



SUMMARY

In hindsight, the last forty years have been an exciting time for tobacco chemists working in the area of menthol analysis. As the tobacco industry, mentholated cigarettes and consumers have each evolved, the analyst has been faced with new questions, problems and challenges. Many different analysis approaches have been necessary to address the diverse chemical questions and varied analysis constraints which have been posed. Fortunately, due to rapid advances in chemical measurement instrumentation coupled with personal creativity and innovation, tobacco chemists have prevailed.

Menthol analysis promises to provide continuous challenge for the immediate future. Method accuracy and precision improvements will continue to be a goal. However, with current sample volume demands and the prevailing economic climate, simplification of sample preparation and improved analysis throughput will be areas of primary emphasis.

Additional laboratories may adopt the total automation approach to sample analysis which Philip Morris has pursued. More likely, semiautomation will be exploited to simplify sample preparation and increase throughput.

Finally, several analysis techniques have either been largely ignored or only investigated in a cursory fashion for the determination of menthol. Headspace gas chromatography is ideally suited to the determination of menthol. Refinement of headspace GC instrumentation during the last 5 to 10 years provides an opportunity for renewed application of this technique in a high volume analysis mode. The use of near infrared reflectance spectroscopy (20) and supercritical fluid extraction (29) are further examples of analysis techniques for which the full potential has not yet been realized. The tobacco chemist should keep in mind a thought from a recent television commercial when considering the investigation of these and other techniques, "Your only limits are the size of your dreams and the degree of your dedication to them" (3).

ACKNOWLEDGEMENTS

I am grateful to my colleagues at R. J. Reynolds who have contributed to this work in many ways. They are both a source of inspiration and a pleasure to work with. I appreciate the time and effort Mr. Ken Beard spent preparing the apparatus figures. He is truly an artist disguised as an analytical chemist. I am also very grateful for the kindness and assistance of Ms. Marian DeBardeleben of Philip Morris who provided some otherwise difficult to find literature. Finally, the patience and counsel of Dr. Tom Perfetti will always be fondly remembered.

REFERENCES

1. Anonymous. 1968. Changes in official methods of analysis made at the 81st annual (A.O.A.C.) meeting, 1967. VI. Plants. *Journal of the Association of Official Analytical Chemists*. 51(2):447-449.

2. Anonymous. 1932. Spuds. *Fortune*. 6:51.

3. Apple Computer Company. *Apple Computer's - Industrial Revolution: The Power to be Your Best.* A television commercial available from Radio/TV Reports, 41 East 42nd Street, New York, New York.

4. Baldinger, L. H. 1942. The analysis of peppermint oil. *Industrial and Engineering Chemistry. Anlytical Edition.* 14(1):15-20.

5. Beard, K. A. and Hicks, R. D. 1991. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

6. Best, F. W. 1987. Radiotracer studies with carbon-14 labeled glycerol: fate in total smoke. *Proceedings of the International Conference on the Physical and Chemical Processes Occurring in a Burning Cigarette.* April 26-29, 1987, Graylyn Conference Center of Wake Forest University, Winston-Salem, North Carolina, pp 244-260.

7. Borgerding, M. F., Beard, K. A., Stennis, V. B., Treadaway, A. R. and Moreland, R. J. 1993. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

8. Borgerding, M. F., Dunn, R. S. and Gordon, B. M. 1982. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

9. Borgerding, M. F., Fowler, K. W., LaMachio, M. M., Morrison, C. C., Parsons, S. V. and Winkler, L. S. 1993. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

10. Borgerding, M. F., Hicks, R. D., Bodnar, J. E., Riggs, D. M., Nanni, E. J., Fulp, Jr., G. W., Hamlin, Jr., W. C. and Giles, J. A. 1990. Cigarette smoke composition. Part 1. Limitations of FTC method when applied to cigarettes that heat instead of burn tobacco. *Journal of the Association of Official Analytical Chemists.* 73(4):605-609.

11. Borgerding, M. F., Milhous, Jr., L. A., Hicks, R. D. and Giles, J. A. 1990. Cigarette smoke composition. Part 2. Method for determining major components in smoke of cigarettes that heat instead of burn tobacco. *Journal of the Association of Official Analytical Chemists.* 73(4):610-615.

12. Brignall, T. W. 1941. Determination of menthol in oil of peppermint. *Industrial and Engineering Chemistry. Analytical Edition.* 13(3):166-169.

13. Brozinski, M., Dolberg, U. and Lipp, G. 1972. Untersuchungen uber die verteilung des menthols auf tabak, filter und rauch von mentholcigaretten. *Beiträge zur Tabakforschung International*. 6(3):124-130.

14. Carol, Jonas. 1955. Report on infrared spectrophotometric methods for drugs. *Journal of the Association of Official Agricultural Chemists*. 38(3):638-643.

15. Carpenter, R. D. and Seligman, R. B. 1956. The determination of menthol cigarette filler. 10th Tobacco Chemists' Research Conference, Washington, D. C., Paper No. 9.

16. Christensen, B. E. and Pennington, L. 1942. Determination of menthol in oil of peppermint. *Industrial and Engineering Chemistry. Analytical Edition*. 14:54-55.

17. Core, M. T., Logue, M. and Haut, S. A. 1980. Separation of menthols and menthones by normal phase high performance liquid chromatography. 34th Tobacco Chemists' Research Conference, Richmond, Virginia, Paper No. 18.

18. Curran, J. G. 1972. Delivery of menthol from cigarettes containing either a mentholated filter or mentholated tobacco. *Tobacco Science*. 16:40-42.

19. Curran, J. G. 1975. Effect of certain liquid additives on menthol delivery. *Tobacco Science*. 19:69-70.

20. Diffee, J. T. 1992. Chapter 16. Tobacco analysis by NIR spectroscopy. Handbook of Near-Infrared Analysis (D. A. Burns and E. W. Ciurczak, Editors). Marcel Dekker, Incorporated, New York.

21. Emberger, R. and Hopp, R. 1985. Synthesis and sensory characterization of menthol enantiomers and their derivatives for the use in nature identical peppermint oils. Topics in Flavour Research (R. G. Berger, S. Nitz and P. Schreier, Editors). H. Eichhorn, Hangenham, Germany.

22. Frank, M. S. 1983. The rapid quantitative determination of menthol in tobacco. 37th Tobacco Chemists' Research Conference, Washington, D. C., Paper No. 36.

23. Frank, M. S. and Lin, O. C. 1987. The analysis of propylene glycol, menthol, triacetin, glycerin, and triethyleneglycol diacetate in cigarettes. 41st Tobacco Chemists' Research Conference, Greensboro, North Carolina, Paper No. 47.

24. Gains, L. H. and Marmor, R. S. 1987. Sensory evaluation of sidestream odor using transfer testing methodology. *Beiträge zur Tabakforschung International*. 14(1):53-59.

25. Gillen, D. G. and Scanlon, J. T. 1972. The separation of menthol-menthone stereoisomers. *Journal of Chromatographic Science*. 10:729-732.

26. Gordon, B. M. and Borgerding, M. F. 1981. A rapid gas chromatographic determination of menthol in tobacco. 35th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina, Paper No. 38.

27. Harrell, T. G. 1956. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

28. Haut, S. A. and Core, M. T. 1981. Separation of menthol isomers by normal phase high performance liquid chromatography. *Journal of Liquid Chromatography*. 4(10):1869-1874.

29. Hawthorne, S. B., Krieger and M. S., Miller, D. J. 1988. Analysis of flavor and fragrance compounds using supercritical fluid extraction coupled with gas chromatography. *Analytical Chemistry*. 60(5):472-477.

30. Hicks, R. D. 1988. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

31. Hicks, R. D. and Dunlap, S. P. 1993. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

32. Hughes, L. F. September 29, 1925. Process of treating cigarette tobacco. U. S. Patent No. 1,555,580.

33. Jenkins, Jr., R. W., Newman, R. H. and Chavis, M. K. 1970. Cigarette smoke formation studies. II. Smoke distribution and mainstream pyrolytic composition of added ^{14}C-menthol (U)*. *Beiträge zur Tabakforschung International*. 5(6):299-301.

34. Jenkins, Jr., R. W., Chavis, M. K., Newman, R. H. and Morrell, F. A. 1971. The quantitative recovery of smoke from radioactively labeled cigarettes. *International Journal of Applied Radiation and Isotopes*. 22:691-697.

35. Johnson, R. R. 1972. Comparison of D- and L-menthol as cigarette flavorants. 26th Tobacco Chemists' Research Conference, Williamsburg, Virginia, Paper No. 27.

36. Jones, J. S. and Fang, S. C. 1946. Determination of menthol in peppermint oil. *Industrial and Engineering Chemistry. Analytical Edition.* 18:130-131.

37. J&W Scientific. 1992-1993. Product Catalog and Reference Guide. J&W Scientific, Folsom, California, p 122, 132.

38. Kaburaki, Y., Mikami, Y. and Kuniyoshi, H. 1966. Simultaneous determination of menthol and triacetin in filter plugs by gas chromatography. Scientific Papers of Central Research Institute Japan Monopoly Corporation, 108, pp 179-184.

39. Kobashi, Y. and Yamashita, Y. 1965. Studies on menthol cigarettes II, thermal analysis of menthol and menthol derivatives. Nippon Senbai Kosha Chuo Kenkyusho Kenkyu Hokoku, 107, pp 295-298.

40. Kusama, M., Arai, S. and Ikegami, S. 1964. Gas chromatographic determination of menthol in mentholated cigarette flavor. Scientific Papers of Central Research Institute Japan Monopoly Corporation, 106, pp 137-139.

41. Lemli, J. A. J. 1954. Determination of menthone, menthol, and menthofuran in peppermint oil. *Annales Pharmaceutiques Francaises.* 12:275-281.

42. Lubus, J. J. and Bogue, H. D. 1960. The determination of menthol in mentholated cigarettes. *Tobacco Science.* 4:213-215.

43. Lyerly, L. A. 1967. Direct vapor chromatographic determination of menthol, propylene glycol, nicotine and triacetin in cigarette smoke. *Tobacco Science.* 11:49-51.

44. Marshall, C. V. 1969. Report of subcommittee A on recommendations of referees. *Journal of the Association of Official Analytical Chemists.* 52(2):322-324.

45. Masamune, H. 1933. Biochemical studies on carbohydrates. II. A micro colorimetric method of determination of free and conjugated menthol in blood and tissues. *Journal of Biochemistry.* 18(2):277-283.

46. McMurtrie, A. and Canon, A. B. 1979. Rapid, quantitative determination of menthol/triacetin in smoke. 33rd Tobacco Chemists' Research Conference, Lexington, Kentucky, Paper No. 39.

47. Mickey, D. D., 1990. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

48. Mitchell, B. C., Barbee, E. P. and Irby, Jr., R. M. 1963. The chromatographic determination of menthol in cigarettes and cigarette smoke. *Tobacco Science.* 1:64-66.

49. Moore, D. R. and Kossoy, A. D. 1961. Quantitative analysis of menthol stereoisomers by gas-liquid chromatography. *Analytical Chemistry.* 33(10):1437.

50. Morrell, F. A. and Varsel, C. 1966. Total combustion product cigarette smoking machine-analyses of radioactive cigarette paper. *Tobacco Science.* 10:45-50.

51. Nelson, E. K. 1936. Report on oil of peppermint. *Journal of the Association of Official Agricultural Chemists.* 19:529-532.

52. Nesemann, E. and Seehofer, F. 1972. Zur bestimmung von tabakadditiven. *Beiträge zur Tabakforschung International.* 6(3):131-133.

53. Neurath, G. and Ehmke, H. 1964. Apparatur zur untersuchung des nebenstromrauches. *Beiträge zur Tabakforschung International.* 2(4):117-121.

54. Newman, R. H., Jones, W. L. and Jenkins, Jr., R. W. 1969. Automatic device for the evaluation of total mainstream cigarette smoke. *Analytical Chemistry.* 41(3):543-545.

55. Official Methods of Analysis. 1990 (15th Edition). Menthol in cigarette filler (colorimetric method). Association of Official Analytical Chemists, Arlington, Virginia, Method No. 968.02.

56. Official Methods of Analysis. 1990 (15th Edition). Menthol in cigarette filler (gas chromatographic method). Association of Official Analytical Chemists, Arlington, Virginia, Method No. 968.03.

57. Official Methods of Analysis. 1990 (15th Edition). Nicotine on Cambridge filter pads (gas chromatographic method). Association of Official Analytical Chemists, Arlington, Virginia, Method No. 979.01.

58. Proctor, C. J., Martin, C., Beven, J. L. and Dymond, H. F. 1988. Evaluation of an apparatus designed for the collection of sidestream tobacco smoke. *Analyst.* 113:1509-1513.

59. Riehl, T. F., Shockley, L. L. and Reynolds, M. L. 1973. Menthol distribution and transfer. *Tobacco Science.* 17:10-11.

60. Rodd, E. H. 1968. Rodd's Chemistry of Carbon Compounds, Volume II Part B (S. Coffey, Editor). Elsevier Publishing Company, New York.

61. Shoffner, R. A. and Ireland, M. S. 1982. Rapid analysis of menthol and nicotine in smoke and the effects of air dilution on delivery. *Tobacco Science.* 26:109-112.

62. Smith, Jr., R. C., Lewis, A. and Clauson, D. W. 1993. "The school for innovators." *The Office of Strategic Innovation.* Houston, Texas.

63. Thornton, R. E. and Valentine, C. 1968. Determination of the balance of carbon-14 activity added to cigarettes. *Beiträge zur Tabakforschung International.* 4(7):287-292.

64. Tucker, C. L. and Ogg, C. L. 1966. Menthol in cigarette tobacco filler. *Journal of the Association of Official Analytical Chemists.* 49(6):1283.

65. Tucker, C. L. 1967. Determination of menthol in cigarette tobacco filler. *Journal of the Association of Official Analytical Chemists.* 50(4):770-773.

66. Tucker, C. L. 1968. Determination of menthol in cigarette tobacco filler. *Journal of the Association of Official Analytical Chemists.* 51(3):650-653.

67. Uhrig, M. S., Heckman, R. A. and Davis, N. M. 1982. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina. Unpublished data.

68. Whitaker, T. B. and Dickens, J. W. 1974. Variability of aflatoxin test results. *Journal of the American Oil Chemists' Society.* 51(5):214-218.

69. Yasumatsu, N., Kawabata, M., Iseda, J. and Fukuzumi, T. 1977. Determination of menthol in cigarettes and mainstream smoke condensate. Nippon Senbai Kosha Chuo Kenkyusho Kenkyu Hokoku, 119:23-28.

70. Yoshitani, H., Yamamoto, T., Nishi, H., Wakui, S., Takahara, H., Inumaru, H. and Kamachi, T. 1968. Studies on menthol cigarettes V. Rapid method for the determination of menthol in top dressing material. Scientific Papers of Central Research Institute Japan Monopoly Corporation 110:105-111.

DEDICATION

This manuscript is dedicated to the memory of Dr. Robert A. Heckman. Bob will always be associated with TCRC in my thoughts because he presented a symposium paper at the first TCRC that I attended. Bob passed away unexpectedly as I started work on this manuscript. He was an accomplished scientist and a fine gentleman who is missed by his colleagues.

47th Tobacco Chemists' Research Conference

THEORETICAL ASPECTS OF MENTHOL MIGRATION AND TRANSFER

Steven A. Wilson

Eastman Chemical Company
Research Laboratories
P. O. Box 1972
Kingsport, TN 37662-5150

ABSTRACT

The behavior of menthol in cigarettes during storage and smoking has been extensively studied because of the popularity and the unique properties of menthol. Most studies have involved empirical measurements of menthol's migration during storage and transfers during smoking.

It is well known that menthol has significant migration during storage, because of its volatility. In general, the studies have found that menthol seeks a balance between the two major components of the cigarette: the tobacco column and the cellulose acetate filter. This balance is influenced by the cigarette construction parameters and has an impact on the transfer into smoke. Studies have shown that the transfer from the tobacco column during smoking is constant with time, but the transfer from cellulose acetate filters changes with time due to diffusion of the menthol into plasticized fibers of the filter.

Some researchers have formulated and tested theories for these behaviors and have been successful at making reasonable predictions. A review of the general behavior and current

theories of the processes occurring within mentholated cigarettes would be valuable, because it allows one to link the results and conclusions from the various studies. This paper discusses the current theories that describe the characteristics of menthol's migration and transfer in cigarettes.

INTRODUCTION

Because of menthol's popularity and unique properties, several groups have studied the behavior of mentholated cigarettes. This paper reviews results of key studies and the current theories that describe the characteristics of menthol's migration and transfer in cigarettes.

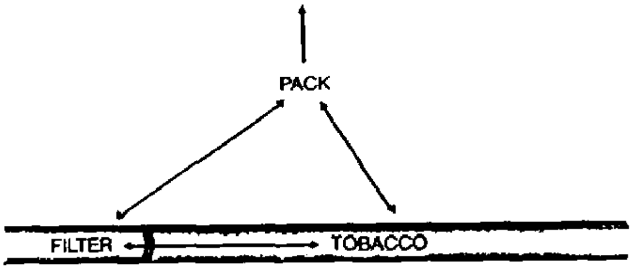
For an area of study to make significant advances, researchers must continually test theories against experimental data. A quote on this experimentation process by a pioneer in analytical chemistry, Dr. I. M. "Piet" Koltoff, is "Theory guides, experiment decides" (34). As theories are reviewed against experimental results, they are refined and improved, thereby allowing for more focused experiments. This review should be useful for clarifying our understanding of mentholated cigarettes and also for understanding the general behavior of other volatile additives in cigarettes.

There are two sections to this paper. The first section covers the migration and diffusion phenomena that occur during storage of mentholated cigarette products. The second section covers the transfer of menthol into and out of the aerosol during cigarette smoking. The results from key studies will be presented which describe the behavior of mentholated cigarettes in order to test the current theories.

MIGRATION DURING STORAGE

The migration of menthol in cigarettes has been studied several times since it was first learned that menthol migrates between the various components in a pack of cigarettes. There are a number of parameters which influence menthol's migration and several studies have evaluated these influences (8, 11, 12, 13, 14, 15, 17, 24, 27, 28, 30, 31, 32, 37, 38). Menthol has an affinity for both the tobacco column and cellulose acetate filter tips and will migrate from one to the other during storage (Figure 1). Some menthol will reside on the paper or packaging material, but the amount is small (< 5%) and does not change with time (e.g., 32 or 28).

FIG. 1
Menthol Migration



Curran in 1973 and 1975 (12, 13) and Wood in 1983 (38) studied the effects of construction variables of cellulose acetate filters on the migration of menthol. Filters employing cellulose acetate fibers can be assembled with various fiber sizes and cross sections, numbers of fibers, and weights to generate the filtration efficiency and pressure drop required. When making a filter, a solvent or plasticizer which dissolves into cellulose acetate is sprayed onto the fibers to bond them and increase the firmness of the filter tip. The most common plasticizers are triacetin, triethylene glycol diacetate (TEGDA) and polyethene gylcol 600 (PEG 600). Curran studied the liquid filter additive variables of: the amount and type of plasticizer; the addition of 1,2-propanediol or glycerol; and the effect of filter surface area on the migration from the tobacco column to the filter. Wood studied the effects of plasticizer type and level, and the effects of denier per filament and total denier. Both Curran and Wood found that the level of plasticizer was the most important parameter, followed by the type of plasticizer. More menthol migrated to filters bonded with TEGDA than with triacetin, resulting in less menthol delivery upon smoking. Curran found no correlation between surface area and migration, while Wood found that the filter's affinity for menthol increased with denier per filament and total denier.

In a recent study, Renfro evaluated the effect of triacetin on the migration to a filter (28). The presence of

7% triacetin significantly increased the amount of menthol on the filter (Figure 2) compared to no plasticizer (Figure 3). The results from this study, lasting almost a year, are representative of the migration behaviors that occur in tobacco column menthol applications.

FIG. 2

Menthol Distribution (Renfro, 1990)

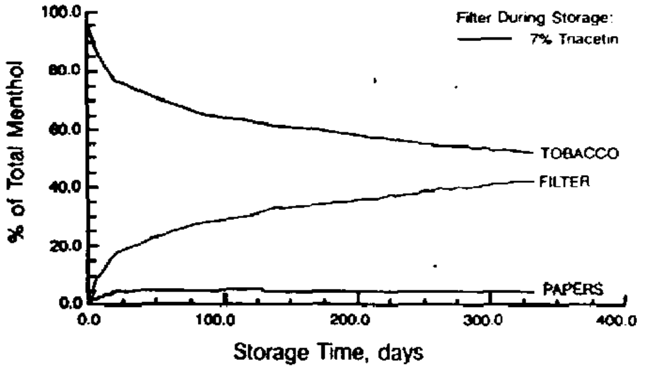
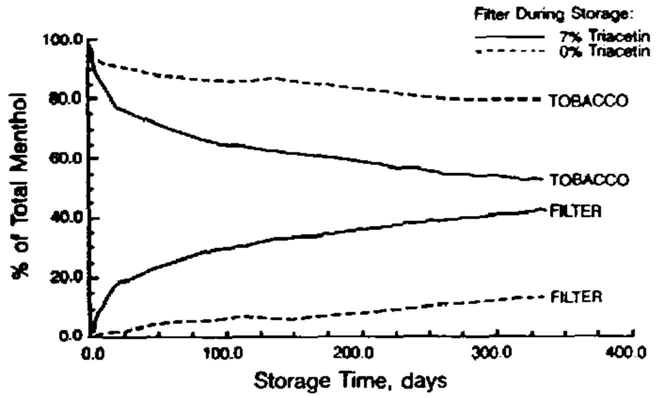


FIG. 3

Menthol Distribution (Renfro, 1990)



In 1983, Mathis reported a study of the migration, from the filter tip to the tobacco column, and delivery of several volatile flavorants added to the filter (20). The rate of migration of the model flavorants was determined to obey first-order kinetics, with the rate constant being determined by the volatility of the flavors dissolved in the plasticized fibers of the filter. The migration can be characterized by curve fitting the following equation to the migration data:

$$M(t) = M_{eq}\,(1 - e^{-kt})$$

Where: $M(t)$ = Migration level at time t
M_{eq} = Migration level at equilibrium
e = Natural base
k = First order rate constant
t = Time

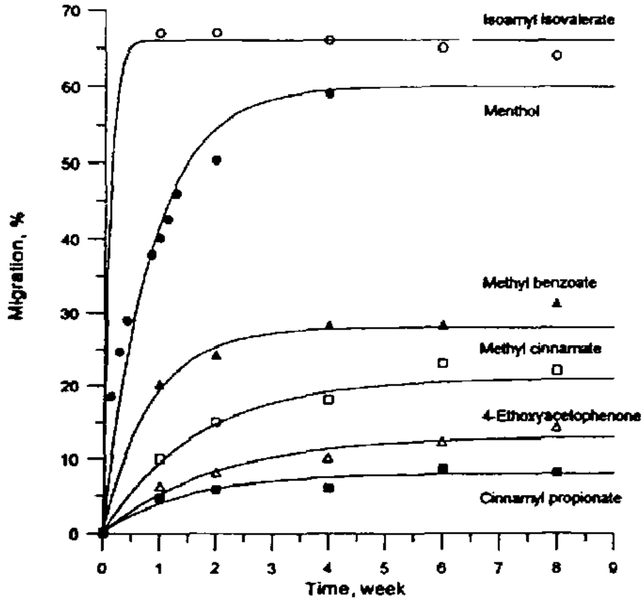
This interpretation of migration data allows for an estimate of the half life and equilibrium level of volatile flavorants (Table I and Figure 4).

TABLE I

Kinetics Of Filter Flavor Migration (Mathis 1983)

Flavor	$v^{0.01}_{25}$	P^0_{25} (Torr)	$v^{0.01}_{25}P^0_{25}$ (Torr)	k (Week^{-1})	t (Week)	M_{eq} (%)
Isoamyl Isovalerate	6.72	0.9	6.05	≥ 8.98	≤ 0.077	66 ± 2
Methyl Benzoate	1.05	0.4	0.42	1.18 ± 0.15	0.59	28 ± 2
Methyl Cinnamate	0.79	0.26	0.21	0.60 ± 0.27	1.2	21 ± 2
4-Ethoxy-Acetophenone	1.39	0.004	0.0056	0.51 ± 0.38	1.4	13 ± 2
Cinnamyl Propionate	0.97	0.002	0.0019	0.68 ± 0.40	1.0	8 ± 1
Cinnamyl Isovalerate	1.36	0.001	0.0014	0.33 ± 0.33	2.1	16 ± 5
Menthol	10.4	0.1	1.4	1.20 ± 0.10	0.58	60 ± 1

FIG. 4
Migration Of Flavors (Mathis, 1983)



This study pointed out that, since a flavorant's vapor pressure is affected by its environment or surroundings, any change in a component of a cigarette which would affect menthol's vapor pressure will influence the migration rate and equilibrium level. Therefore, any modification of a cigarette which affects the vapor pressure of the additives would likely affect the ultimate performance.

There are two theories for why the addition of a plasticizer affects the menthol migration rates and equilibration levels in filter tow filters. The first is based upon a thermodynamic viewpoint, in which the plasticizer increases the solubility of the filter for menthol, and therefore increases the affinity of the filter for menthol. The second is based upon a kinetic viewpoint, in which the plasticizer increases the diffusion rate into the fibers, which increases the amount of menthol which is absorbed into the filter during the study time.

Taking the thermodynamic viewpoint, the balance or equilibrium level between the tobacco column and filter tip is affected by the affinities of each for menthol. Insight into the ability for compounds to mix can be gained from comparing the Hildebrand solubility parameters. This measure of solubility is based upon the *cohesive* energy (the energy of interaction in a substance) per unit volume (4). Table II lists the Hildebrand solubility parameters for typical cigarette components. Substances with similar solubility parameters are soluble in one another (29). As expected, the typical plasticizers used in filters, triacetin, TEGDA, and PEG 600 are similar to cellulose acetate. Note also, that the solubility parameter for menthol is close to cellulose acetate, indicating that there should be good solubility. In a study by Brozinski *et al.* in 1972, it was found that the cellulose acetate filters had 4.5 times the affinity for menthol compared to the tobacco column (8). This greater affinity for the filter is supported by the solubility parameters, since tobacco's solubility is believed to be similar to glycerol which is significantly different from menthol (21). The poor solubility of menthol in the tobacco column causes menthol not to readily absorb into the tobacco column (4, 5, 16).

TABLE II

Solubility Parameters

Compound	Hildebrand Units
Menthol	9.7
Triethylene Glycol Diacetate (TEGDA)	10.1
Triacetin	10.7
Polyethene Glycol 600 (PEG 600)	10.7
Cellulose Diacetate	11.7
Propylene Glycol	14.8
Glycerol	17.7
Water	23.4

From the kinetic viewpoint, the diffusion rate into cellulose acetate fiber is the rate limiting step. Data in Table III show the diffusion rate of wate in various media and show that the diffusion rates of small molecules into polymers are significantly slower than in a liquid or air. The presence of a plasticizer in a polymer will increase the diffusion rate and therefore the migration rate.

Diffusion in most media is Fickian in behavior with the diffusion coefficient being constant and the rate being proportional to the square root of time. There is an exception in the case of a solvent dissolving into a glassy polymer. This type is called Case II diffusion behavior and is unique to glassy polymers below their glass transition temperature, t_g (9, 36). This diffusion is characterized by a sharp solvent front compared to the gradual changing front of Fickian diffusion. The sharp front is caused by the solvent or plasticizer affecting the diffusion rate in the polymer, i.e., the diffusion coefficient. The polymer molecules are freer to move with the plasticizer present than without plasticizer. In Case II diffusion, the penetration of the solvent or plasticizer is proportional to the amount of small molecules and temperature.

TABLE III

Comparison Of Diffusion Rates In Various Media

Media	Water Diffusion Coefficient At 25°C (cm^2/sec)
Air	0.25
Water	0.000024
Polymer	
Poly (Ethyl Methacrylate)	0.000000102
Poly (Vinyl Chloride)	0.000000024
Lexan	0.00000068

An example of the diffusion effects of plasticizers and heating is the manufacturing of steam cured filters in which the steam gives heat and water which allows for the rapid forming of filters. The increased rate of diffusion is also seen when heating plasticizied filters. The plasticizer concentration in the heated filters changes little, while the plasticizer transferred upon smoking is measurably reduced, because the plasticizer has diffused further into the fibers. In the case of mentholated cigarettes, heating the filter causes deeper penetration of the plasticizer and menthol into the filter, thus reducing the amount of plasticizer or menthol which can transfer into the smoke.

Recent advances in spectroscopic techniques may allow the direct measurement of the diffusion processes in a plasticized filter in the future. Koenig's research group at Case Western University has shown the feasibility of observing the diffusion of small molecules, such as solvents, into polymers by pulsed two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy (19, 35, 36).

Mathis, at the Tobacco Chemists' Research Conference (TCRC) in 1990, presented a computer model which simulates behavior of menthol (21). The model was a "finite difference simulation" which approximated the migration and diffusion processes. The model is based upon Fick's law of diffusion and a variation of Henry's law to estimate volatility. Fick's law describes the flux of a substance, such as menthol:

$$F = -D\,(dC/dx)$$

Where: F = Flux of menthol per unit area per second
D = Diffusion coefficient of menthol, cm^2/second
C = Concentration of menthol, mole/cm^3
x = Distance, cm

Henry's law governs the vapor pressure of ideal mixtures. A variation of Henry's law for nonideal mixtures includes the addition of activity coefficients and allows one to compensate for the nonideal nature:

$P = \gamma X P^\circ$

Where: P° = Solution vapor pressure of menthol

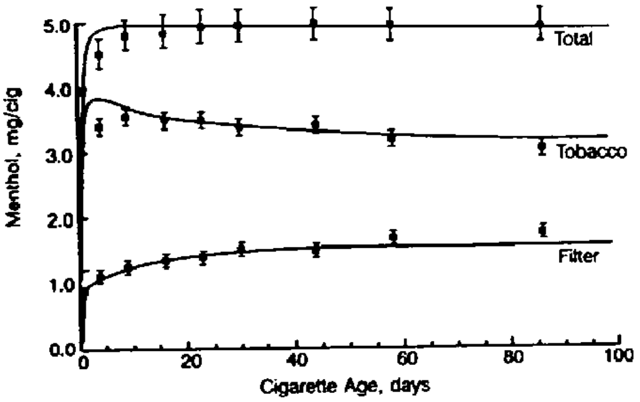
γ = Activity coefficient of menthol

X = Mole fraction of menthol in solution

P^* = Vapor pressure of pure menthol

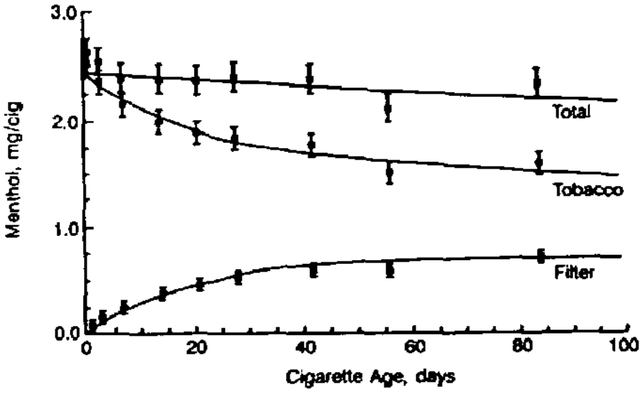
Using these two equations, this model was able to simulate the migration seen in the foil application study reported by Strickler et al. in 1991 (32), Figure 5, and the tobacco column application study reported by Renfro in 1990 (28), Figure 6.

FIG. 5
Simulation Of Menthol Migration (Mathis, 1990)
(Pack Application Case)



All published menthol studies have been with cigarettes that were either unfiltered or filtered with cellulose acetate based filter tow. But from first principles, one can estimate the migration behavior of specialty filtered cigarettes. In the use of molded cigarettes with high plasticizer levels present, one would expect an increase in the level of menthol on the filter due to the plasticizer, and the increase is affected by the heat history of the filter which would influence the diffusion rates. If the surface area in the filter is significantly increased, such as by using activated charcoal, then an increase in migration would also be expected.

FIG. 6
Simulation Of Menthol Migration (Mathis, 1990)
(Tobacco Application Case)



TRANSFERS DURING SMOKING

There are several processes which occur during the smoking of a cigarette. In addition to the dynamic environment of the burning fire cone, there is filtration and condensation onto the tobacco column, as well as filtration and condensation by the filter tip, and transfers into the smoke. The processes occurring during puffing and smouldering are illustrated in Figure 7 and Figure 8.

Tobacco Column - Fire Cone And Condensation

Extensive research has been conducted to understand the dynamics of the burning tobacco column, i.e., the fire cone. Baker wrote an extensive review of these studies in 1981 (3). His review highlighted that the fire cone has a temperature profile as shown in Figure 9 for the gas phase. The tobacco column is degraded by combustion and pyrolysis during smoking. Combustion occurs at the end and sides of the fire cone, because of the availability of oxygen. Pyrolysis and distillation occur between the fire cone and the tobacco column during puffing, because of the high temperatures of the gases and the lack of oxygen.

FIG. 7
Processes In A Burning Cigarette: Puffing (Baker, 1981)

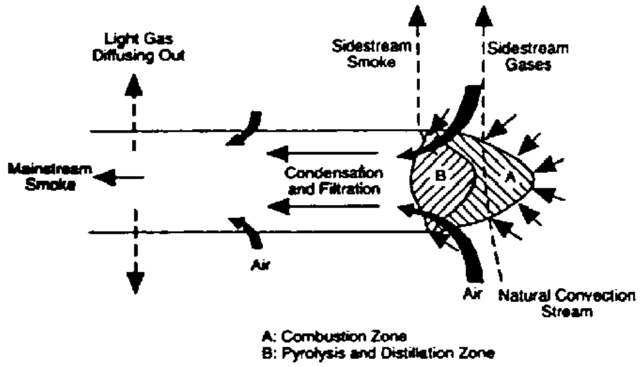


FIG. 8
Processes In A Burning Cigarette: Smouldering (Baker, 1981)

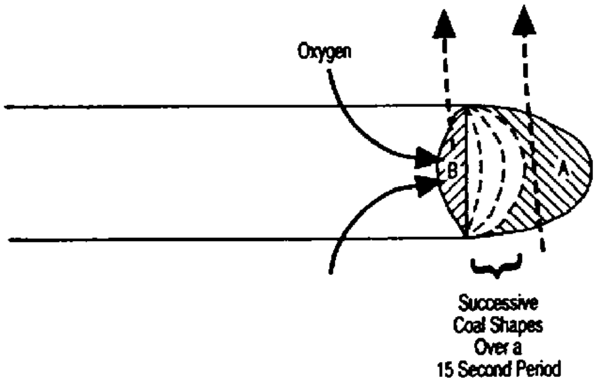
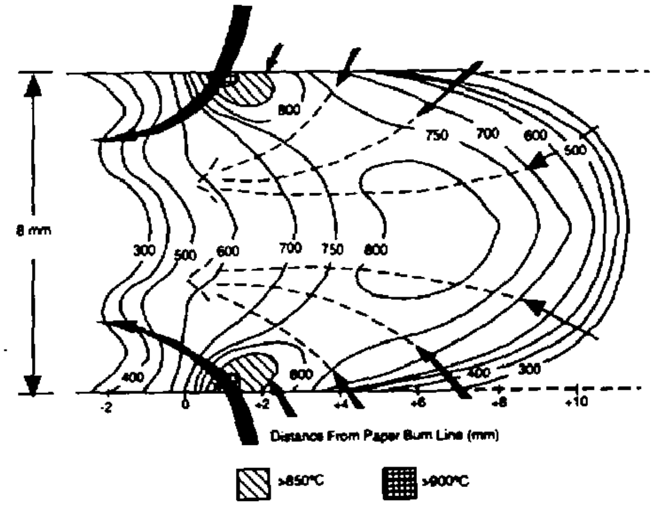


FIG. 9

Temperature (°C) Distribtuion Of Solid Phase In The Coal
1.0 Second After The Start Of A Two Second Puff.
Estimated Air Flow Pattern Into Coal Shown.
Thickness Of Arrow Is Proportional To Magnitude Of Air Flow.
(Baker, 1981)



Jenkins in 1970 (17) and Eble in 1987 (15) studied the fate of radioactively labeled menthol in unfiltered cigarettes (Table IV). They found about half of the radioactivity was in the mainstream smoke, mainly in the TPM with very little in the vapor phase. The rest of the activity was in the sidestream smoke and was roughly evenly distributed between the TPM and gases.

Eble in 1987 (15) and Renfro in 1990 (28) performed experiments using mentholated and nonmentholated tobacco columns to evaluate the transfer of menthol to smoke. In this experiment, one switches the tobacco columns and filter tips from cigarettes which were identically made and aged except for the menthol load. Such an experiment allowed the independent determination of the fate of menthol from the tobacco column and the filter.

TABLE IV

Percent Distribution Of Menthol In Smoke

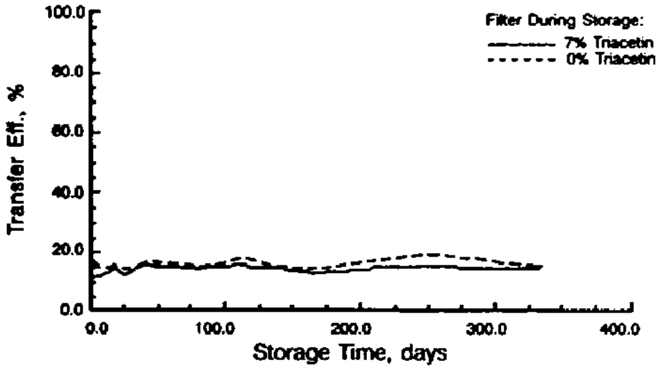
Component	Jenkins (17)	Eble (15)
Mainstream TPM	28	48
Mainstream Gases	1	1
Sidestream TPM	23	17
Sidestream Gases	21	22
Butt	27	8
Ash	-	0
Total	100	96

(Cigarettes were unfiltered)

Renfro found no change in the delivery efficiency of menthol from the tobacco column over time (Figure 10). This result implies that no significant diffusion or interaction occurs with tobacco which would limit the availability of menthol.

FIG. 10

Tobacco Column Menthol (Renfro, 1990)



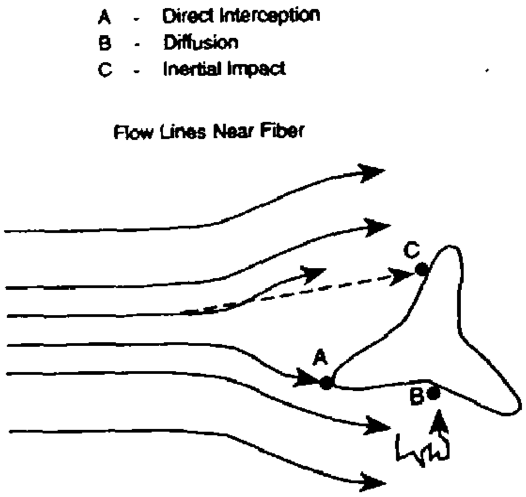
Several research groups have studied the mechanisms of transferring volatile components from the tobacco column into smoke and formulated mathematical models (6, 7, 23, 33). In general, they found two basic processes: (a) elution from the tobacco column, and (b) distillation occurring within 10 mm behind the fire cone.

<u>Filter - Filtration and Elution</u>

The filter plays a key role in the behavior of menthol in a cigarette. Menthol is both filtered and eluted as the smoke flows through the filter.

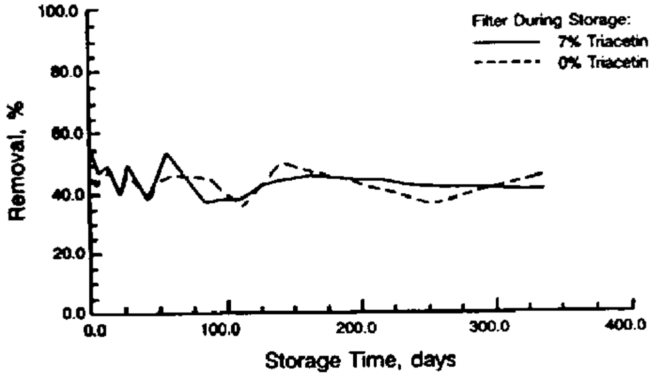
Most of the menthol in the smoke aerosol is removed through the typical mechanisms of smoke filtration, e.g., impaction, diffusion and interception. Several groups have developed models for predicting the 'tar' removal efficiency of cellulose acetate filters (e.g., 18, 26).

FIG. 11
Mechanical Filtration Of Smoke Particles



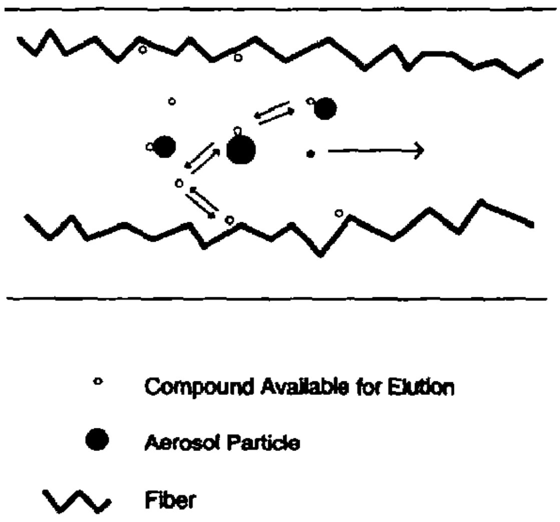
Morie *et al.* in 1975 studied the parameters that affect the selective filtration of several smoke components (1, 22). In general, they found that compounds with sufficient volatility and a high solubility parameter ($\delta > 13$) will be selectively removed from cigarette smoke by filters made with cellulose acetate. Renfro (28) found the selective filtration of menthol to be rather small for both the plasticized and unplasticized filters (Figure 12). Apparently, most of the menthol is retained in the particulate phase.

FIG. 12
Menthol Removal Efficiency (Renfro, 1990)



The elution of flavorants, such as menthol, into smoke is not a simple vaporization process, as shown by the difference in transfers when aerosol is drawn through a cigarette versus hot air. Both Curran in 1973 (12) and Eble in 1987 (15), found that little menthol is transferred from a cigarette's filter when hot dry air is drawn through an unlit cigarette, but significant menthol is transferred with a smoke aerosol. When smoke is present, volatile compounds are believed to vaporize from a fiber and condense onto an aerosol particle, rather than back onto the fiber (Figure 13).

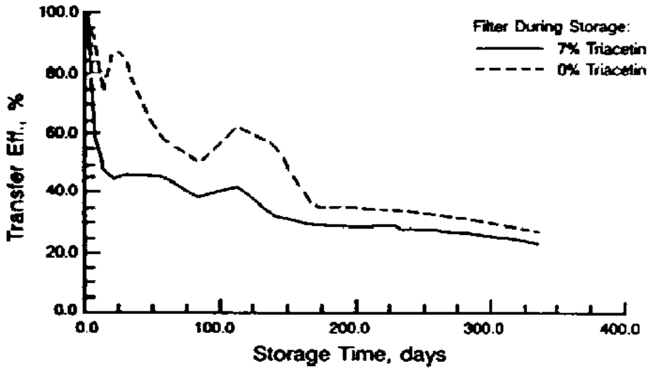
FIG. 13
Elution Of Compounds From A Filter (Renfro, 1990)



Curran *et al.* in 1969 evaluated the factors which influenced the elution of high-boiling compounds (10). He found elution is related to: (a) the vapor pressure of the compound being eluted, (b) the relative affinity between the eluting compound and aerosol, (c) the amount and composition of aerosol, and (d) the temperature of the filter or aerosol.

The elution efficiency from the filter decreases with time (Figure 14). The elution efficiency for menthol from the filter is higher with no plasticizer present, versus with 7% plasticizer, but the amount is lower because less menthol has transferred to the filter. The higher elution efficiency is due to less menthol diffusing into the fiber, because of the low plasticizer level. When the cigarette is smoked, the semivolatiles, i.e., water, condense on the filter during the last few puffs and this may enhance the delivery in addition to warming the filter in the last few puffs.

FIG. 14
Filter Menthol (Renfro, 1990)



Note that the amount of menthol transferred to smoke is higher from the filter than from the tobacco column (filter > 25% versus tobacco < 20%), Figure 10.

Overall Smoke Trends

In aging studies, total menthol delivery from the cigarette increases for approximately one month, then decreases (Figure 15) (31). This response is caused by the migrations, both between the various components in the cigarette pack and out of the pack. Normalizing the amount of menthol transferred into smoke to the amount in the pack, one sees that there is a slow change in efficiency (Figure 16). This result implies that the decrease is not just due to pack loss but also to diffusion into the fiber.

As we have seen, menthol cigarettes will change over time and one key question is what magnitude of change will be noticeable to the smoker. In 1985, Perfetti *et al.* (25) published an extensive study which used "Just Noticeable Difference" (JND) methodology to determine the amount of menthol change that a smoker could perceive. The study's summary results are shown in Table V.

FIG. 15

Menthol Transfer Versus Age (Strickler, 1989)

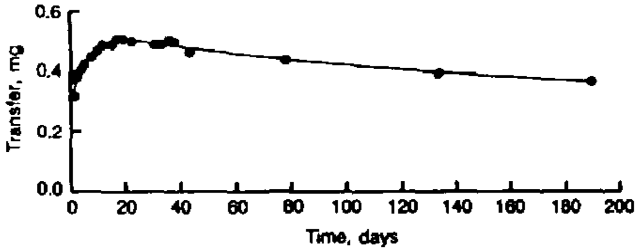


FIG. 16

Menthol Transfer Efficiency Versus Age (Strickler, 1989)

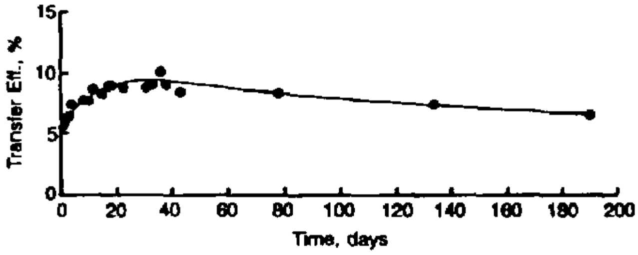


TABLE V

Just Noticeable Differences In Menthol Cigarettes (Perfetti, 1985)

Cigarette Type	JND$_{10}$ (mg/cigarette)
Full Flavor Menthol	± 0.41
Full Flavor Low 'Tar' Menthol	± 0.06
Ultra Low 'Tar' Menthol	- 0.08/+ 0.07

(Cigarettes were made by applying menthol to the tobacco)

SUMMARY

The extensive studies of the migration and transfer of menthol in cigarettes allows the formation and testing of various theories. By reviewing the current theories, we clarify our understanding of the chemical system called mentholated cigarettes. The following generalizations can be made about menthol cigarettes:

a. Menthol is a highly volatile flavorant which migrates to the various components of a cigarette pack during storage.

b. Menthol will continue to seek a balance between the tobacco column and filter tip, but will take several months to approximate an equilibrium.

c. The migration to the filter is controlled primarily by the plasticizer's type and concentration.

d. There is less or slower migration to a filter tip within a given time without plasticizer.

e. Higher levels of plasticizer cause faster migration and higher equilibrium levels on the filter.

f. The migration rate is proportional to the surface area, but the response is smaller than the effect due to plasticizer.

g. The generation of menthol from the tobacco column is constant with time, indicating that there is no significant diffusion process taking place in the tobacco column which would restrict the availability of menthol.

h. There is a relatively high level of menthol transferred into the mainstream smoke, due to the high volatility of menthol.

i. There is little selective filtration of menthol by the filter, since the removal efficiency of menthol by the filter is constant with time, independent of plasticizer level, and close to the removal efficiency of 'tar'.

j. The elution of menthol from filters is affected by the plasticizer's concentration and type.

REFERENCES

1. Baggett, M. S. and Morie, G. P. 1974. Selective removal of semivolatile components of cigarette smoke by various filters. Eastman Chemical Company, Filter Technology Report No. 34.

2. Baker, R. R. 1974. Temperature distribution inside a burning cigarette. *Nature.* 247:405-406.

3. Baker, R. R. 1981. Product formation mechanisms inside a burning cigarette. *Progress in Energy and Combustion Science.* 7:135-153.

4. Barton, A. F. M. 1990. Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters. CRC Press, Boca Raton, Florida, p 88.

5. Barton, A. F. M. 1983. CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press. Boston, Massachusetts, pp 160-161.

6. Bingham, M. A., Craig, J. J. D. and McKeivor, R. 1979. Transfer of additives to mainstream cigarette smoke. 33rd Tobacco Chemists' Research Conference, Lexington, Kentucky.

7. Boyd, D. F. and Craig, J. J. D. 1978. Mathematical model of distillation in tobacco cigarettes. 32nd Tobacco Chemists' Research Conference, Montreal, Canada.

8. Brozinski, M., Dolberg, U. and Lipp, G. 1972. Distribution of menthol in the tobacco, filter and smoke from menthol cigarettes. *Beiträge zur Tabakforschung International.* 6:124-130.

9. Crank, J. and Park, G. S. 1968. Diffusion in Polymers. Academic Press, New York, New York, pp 141-163.

10. Curran, J. G. and Miller, E. G. 1969. Factors influencing the elution of high-boiling components of cigarette smoke from filters. *Beiträge zur Tabakforschung International.* 5:64-70.

11. Curran, J. G. 1972. Delivery of menthol from cigarettes containing either a mentholated filter or mentholated tobacco. *Tobacco Science.* 16:40-42.

12. Curran, J. G. 1973. The effect of filter surface area, filter weight, plasticizers, plasticizer concentration, and storage time on menthol migration from the tobacco to an acetate filter of a filter cigarette. Eastman Chemical Company, Filter Technology Report No. 21.

13. Curran, J. G. 1975. Effect of certain liquid filter additives on menthol delivery. *Tobacco Science.* 19:69-70.

14. Deutsch, L. J. 1990. Menthol behavior in the filter cigarette: the dependence of menthol migration and delivery on the site of application. 44th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina, Abstract 17, p 19.

15. Eble, A. S. 1987. The effects of migration and elution on menthol delivery in cigarettes. *Proceedings of the International Conference on the Physical and Chemical Processes Occurring in a Burning Cigarette.* R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina, pp 261-279.

16. Hildebrand, J. H., Prausnitz, J. M. and Scott, R. L. 1970. Regular and Related Solutions. Van Nostand-Reinhold, Princeton, New Jersey.

17. Jenkins, Jr., R. W., Newman, R. H. and Chavis, M. K. 1970. Cigarette smoke formation studies. II. Smoke distribution and mainstream pyrolytic composition of added uniformly labeled ^{14}C-menthol. *Beiträge zur Tabakforschung International.* 5:299-301.

18. Kao, J. 1990. Practical modeling of filter filtration efficiency. *Beiträge zur Tabakforschung International.* 14:341-352.

19. Koenig, J. L. 1992. Spectroscopy of Polymers. American Chemical Society, Washington, D. C.

20. Mathis, D. E. 1983. Migration and delivery of filter flavors. *Beiträge zur Tabakforschung International.* 12:1-8.

21. Mathis, D. E. 1990. Computer simulation of menthol migration and delivery. 44th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina, Abstract 58, p 41.

22. Morie, G. P., Sloan, C. H. and Baggett, M. S. 1975. Parameters affecting the selective filtration of certain tobacco smoke components. *Beiträge zur Tabakforschung International.* 8:145-149.

23. Muramatsu, M., Umemura, S. and Okada, T. 1979. A mathematical model of evaporation-pyrolysis processes inside a naturally smoldering cigarette. *Combustion and Flame.* 36:245-262.

24. Park, J. Y., Yang, K. K. and Yu, K. K. 1979. A study on the effect of menthol added to filter. *Journal of the Korean Society of Tobacco Science.* 1-2:149-151.

25. Perfetti, T. A. and Gordin, H. H. 1985. Just noticeable difference studies of mentholated cigarette products. *Tobacco Science*. 20:57-66.

26. Rasmussen, G. T. 1987. Models of cigarette smoke filtration. *Proceedings of the International Conference on the Physical and Chemical Processes Occurring in a Burning Cigarette*. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina, pp 151-154.

27. Reihl, T. F., Shockley, L. L. and Reynolds, M. L. 1973. Menthol distribution and transfer. *Tobacco Science*. 17:10-11.

28. Renfro, L. W. 1990. Mechanisms of menthol delivery in filter cigarettes. 44th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina, Abstract 57, p 41.

29. Rosen, S. L. 1993. Fundamental Principles of Polymeric Material. John Wiley & Sons, New York, New York, pp 82-115.

30. Shoffner, R. A. and Ireland, M. S. 1982. Rapid analysis of menthol and nicotine in smoke and the effects of air dilution on delivery. *Tobacco International*. 184:62-65.

31. Strickler, D. V. 1989. Effect of age on the menthol and triacetin delivery of mentholated cigarettes. CORESTA Technical Group, Interlaken, Switzerland.

32. Strickler, D. V. and Wilson, S. A. 1991. A comparison of two foil applications methods for adding menthol to cigarettes. 45th Tobacco Chemists' Research Conference, Asheville, North Carolina, Abstract 35, p 32. CORESTA, Smoke-Techno Groups/Reunion Groupes Techno-Fumee, Utrecht, 1991, Abstract S18.

33. Summerfield, M., Ohlemiller, T. J. and Sandusky, H. W. 1978. A thermophysical mathematical model of steady-draw smoking and predictions of overall cigarette behavior. *Combustion and Flame*. 33:263-279.

34. Warner, M. 1989. Happy 95th birthday, Piet Kolthoff. *Analytical Chemistry*. 61:287A-291A.

35. Weisenberger, L. A. and Koenig, J. L. 1989. NMR imaging of solvent diffusion in polymers. *Applied Spectroscopy*. 43:1117-1126.

36. Weisenberger, L. A. 1989. NMR Imaging of Diffusion Processes in Glassy Polymers. Dissertation, Case Western Reserve University, Cleveland, Ohio.

37. Whitton, T. A. and McAdam, K. G. 1991. Factors influencing the transfer of menthol from cellulose acetate filters. 45th Tobacco Chemists' Research Conference, Asheville, North Carolina, Abstract 34, p 31.

38. Wood, C. E. 1983. Cellulose acetate filter and fiber parameters affecting cigarette menthol delivery and menthol absorption by the filter tip. 37th Tobacco Chemists' Research Conference, Washington, D. C., Abstract 29, p 14.

EFFECTS OF SOME CIGARETTE CONSTRUCTION PARAMETERS ON MENTHOL MIGRATION AND TRANSFER

Fred W. Best

R. J. Reynolds Tobacco Company
Bowman Gray Technical Center
P.O. Box 1487
Winston-Salem, NC 27102

ABSTRACT

In the early days of mentholated filter cigarettes, 'tar' yield was high and menthol transfer to mainstream smoke was fairly efficient. Filters were undiluted and generally inefficient. Early fate studies determined the distribution of menthol to mainstream smoke and filter and/or butt to be greater than 50% of the applied menthol. But, modifications to cigarettes to decrease 'tar' also reduced menthol transfer efficiency. Only about 10% (or less) of the menthol in contemporary cigarettes transfers to mainstream smoke. In attempts to find ways to achieve 'tar' reductions with minimum impact on menthol transfer efficiency, the effect of various cigarette components and variations in cigarette construction on menthol transfer has been extensively studied. Filters exert a major influence on menthol transfer to smoke. Effects of filters and variations in filter construction on menthol transfer to mainstream smoke have been the parameters on which most studies focused. This report will review some of the previously reported research and discuss some previously unreported findings. Effects of a tobacco humectant, propylene glycol, and of five different individual tobacco blend components on menthol migration and transfer are also discussed.

INTRODUCTION

It is impractical in a paper of this type to attempt to cover all of the published data relating to cigarette construction parameter effects on menthol migration and transfer to smoke. This report will review some of the published work and discuss some previously unpublished studies that address the effects of cigarette construction parameters on menthol migration and transfer. We have used a broad definition of the term construction parameters to include configurational aspects, as well as filter materials, filter additives and differing tobacco types.

Unfiltered mentholated cigarettes were introduced in the 1920's. Until the popularization of cellulose acetate (CA) filter-tipped cigarettes in the 1950's there was little reason to be concerned about menthol migration. Once a filter is added to a mentholated cigarette, migration of menthol to the filter becomes important and transfer to smoke becomes complex. With the rapid rise in sales of filter-tipped cigarettes, tobacco scientists began developing and improving methods for analysis of menthol in blends, filters and smoke. As it turns out, menthol migration to the filter can both enhance and inhibit menthol transfer to smoke. Since menthol transfer to smoke is the desired goal, it became very important to understand the interactions between menthol migration and transfer and, also, to determine how other factors affect menthol transfer to mainstream smoke (MS).

FATE STUDIES OF MENTHOLATED CIGARETTES

Making use of Cambridge filters and gas chromatography, the first analysis of menthol in mainstream smoke (MS) was reported at the 1962 TCRC by Mitchell *et al.* (16). It was found that, with four leading brands of mentholated filter-tipped cigarettes, menthol transfer efficiencies ranged from 19% to 26%. The importance of cigarette construction and configuration parameters was not well known at that time, so there was no disclosure of filter plasticizer levels or age of the cigarettes when smoked. In 1968, Newell et al. used randomly (R) labeled ^{14}C-menthol, to determine the "Fate of Menthol in Cigarette Smoke" for a popular mentholated filter-tipped brand with a prototype total recovery smoking apparatus (17). There was a slight problem; this study only accounted for about 85% of the starting radiolabel. Examination of unpublished fate study data with compounds other than menthol generated by Newell with this technique and system at about that same time, comparison with later unpublished data generated with an improved system on the same compounds, and review of subsequent literature values suggested that the missing radiolabel was related to sidestream smoke (SS) gas collection and analysis. Another possible pitfall, as tactfully pointed out by Jenkins *et al.* (12) was, that this study was performed with nonequilibrated cigarettes. The original data from the Newell *et al.* study and corrected data showing menthol distribution if all of the missing radiolabel were in the SS gas phase are shown in Table I.

TABLE I

Fate Of Menthol In Total Smoke
(Data From Newell *et al.*, 1968, Reference 17)

Fraction	Original Recovered Activity (%)	Corrected* Recovered Activity (%)
MS Solids	42.19	35.90
(Intact Menthol)	(40.67)	(34.61)
MS Gases	0.75	0.64
SS Solids	33.40	28.42
(Intact Menthol)	(30.73)	(26.15)
SS Gases	4.54	18.77
Butts & Filters	19.11	16.27
Ashes	0.07	0.06
Total	99.99	100.01

*Assuming all missing radiolabel was in SS gases

The corrected value of 19% in SS gases is in better agreement with levels of 21% and 17% subsequently reported by

Jenkins *et al.* (12) and Eble (9). The data from the study by Newell *et al.* revealed that at least 35% of the menthol transferred to MS in the particulate phase (solids). This was a very efficient transfer, but remember those were the days of inefficient nonair diluted filters. Most importantly, it was determined by inverse isotope dilution that 96.4% of the radioactivity in MS solids and 92% of the radioactivity in SS solids was due to intact menthol.

In 1970, Jenkins *et al.* reported the smoke distribution and mainstream smoke pyrolytic composition of added uniformly labeled (U) ^{14}C-menthol from 70 mm nonfiltered cigarettes with 100% accountability of starting radiolabel (12). Their findings are shown in Table II. With gas radiochromatography, it was determined that 98.9% of the radioactivity found in the mainstream total particulate matter (TPM) was due to intact menthol transfer. Allowing for the reported 0.4% menthone impurity in the starting material, this means that only 0.6% to 1% of the applied menthol transferred to mainstream TPM as thermal degradation products. Schmeltz and Schlotzhauer had previously reported high levels of menthol degradation, 22% at 600°C and 84% at 860°C, during pyrolysis experiments (26). The data of Newell *et al.* (17) and Jenkins *et al.* (12) support the contention that in many cases pyrolysis data cannot be used as a predictor of the fate of a material in cigarette smoke.

TABLE II

^{14}C-Menthol Distribution In Total Smoke
(Data From Jenkins *et al.*, 1970, Reference 12)

Smoke Phase	Distribution (%)
Sidestream Gas	21.2
Sidestream TPM	23.1
Mainstream Gas	1.0
Mainstream TPM	27.9
Butt (20 mm)	26.9
Total	100.1

In a more recent radiotracer study, Eble reported the distribution of menthol in total smoke from 66 mm unfiltered cigarettes fitted with cardboard mouthpieces (9). He found 48% of the applied radioactivity in mainstream TPM, 8% in the butts and 0.96% in mainstream gases. It should be noted that Eble's data were based on transfers from the radiolabel zone (about 55 of the 66 mm length), and he only accounted for 95% of the starting radiolabel.

In these three fate studies, only about 1% of the radiolabel was found in mainstream gases (as thermal degradation products). Very efficient menthol transfer to MS was observed.

MS menthol (radioactivity) transfer data for studies conducted by Newell *et al.*, Jenkins *et al.* and Eble are summarized in Table III.

TABLE III

Menthol Transfer To Mainstream Smoke, Fate Studies Summary*

Source	MS TPM	Butt/ Filter	MS Total	
Newell *et al.* (17)	35.9	16.3	52.2	Filtered
Jenkins *et al.* (12)	27.9	26.9	54.8	Unfiltered
Eble *et al.* (9)	48.2	7.8	56.0	Unfiltered

*Values represent percent of total recovered radiolabel

Total mainstream distributions are very similar, but MS TPM levels are vastly different. Also, menthol appears to be a unique or at least an unusual cigarette flavorant because, depending on smoking parameters, it preferentially transfers, predominantly intact, to MS. Including values from the Mitchell *et al.* study, thus far, menthol transfers to MS range from 19% to 48% with the same standard smoking parameters but with different cigarettes. In a study to determine menthol "Just Noticeable Differences" (JND) levels of a range of mentholated products (22), Perfetti and Gordin reported that for full-flavor menthol (FFM), full-flavor low 'tar' menthol

(FFLTM), and ultra low 'tar' menthol (ULTM), average MS menthol yields were 0.54 ± 0.05 mg, 0.52 ± 0.09 mg and 0.30 ± 0.10 mg, respectively (see Table IV). The average applied menthol levels (percent pack menthol) required to achieve these transfers were 0.39% ± 0.05%, 0.67% ± 0.12% and 0.94% ± 0.21%, respectively. These data represent transfer efficiencies of approximately 17%, 10% and 4% for FFM, FFLTM and ULTM, respectively.

TABLE IV

Menthol Transfers From Varying 'Tar' Level Products
(Data From Perfetti And Gordin, 1985, Reference 22)

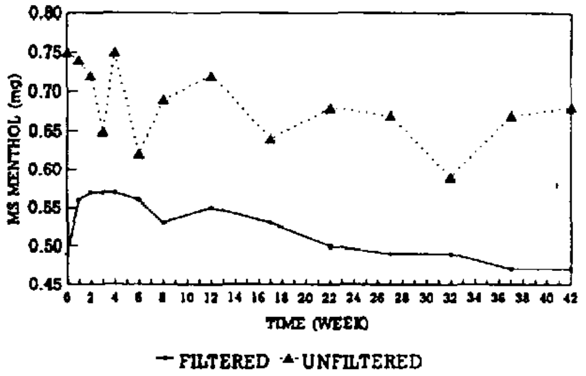
Cigarette	Pack Menthol, %	Transfer, mg	Transfer, %
FFM	0.39	0.54	17
FFLTM	0.67	0.52	10
ULTM	0.94	0.30	4

These are much lower menthol transfer efficiencies compared to the earlier values, and emphasize the fact that configuration and construction parameters, which vary in these products, play significant roles in menthol transfer to MS.

FILTERED VERSUS UNFILTERED CIGARETTES

Significant differences in MS menthol yield patterns over time for filtered and unfiltered cigarettes (see Figure 1) have been reported (1, 9). In an aging study, a commercial king size filtered cigarette with a CA filter plasticized with triacetin gave an extremely low menthol yield at 0-time. On aging, menthol yields increased and peaked somewhere between two and five weeks, after which the yields began declining. For an unfiltered mentholated cigarette, menthol yield was greatest at 0-time and did not exhibit the sharp rise in yield as seen with the filtered products but was rather uniform over time. This suggests the menthol transfer rise and decline is filter related.

FIG. 1
Comparison Of Menthol MS Yields From
Filtered* And Unfiltered Cigarettes
(Data From Best, 1992, Reference 1)

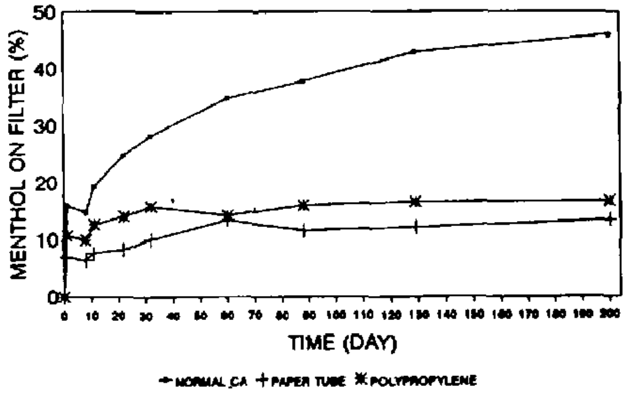


* CA with 7% triacetin

MIGRATION TO DIFFERENT FILTERS

It has been determined that there are differences in menthol migration rates from cigarette rods with different filter types (23). Menthol migration from identical American blend tobacco rods with identical menthol loads (0.66% pack menthol) was much greater to plasticized CA filters (46% after 200 days) than to polypropylene filters (17% after 200 days) as illustrated in Figure 2. A study by Curran (4) revealed that plasticizer was the migration driving force rather than CA. Untreated paper has very low menthol affinity. Menthol migration to paper tube mouthpieces is included in Figure 2 to emphasize the lack of menthol affinity for polypropylene. However, because of their popularity and market domination, most of this discussion will be concerned with effects of CA filters on menthol transfer.

FIG. 2
Menthol Migration To Various Filters
Cellulose Acetate (CA), Polypropylene And Paper Tube
(Data From Perfetti And Teot, 1986, Reference 23)

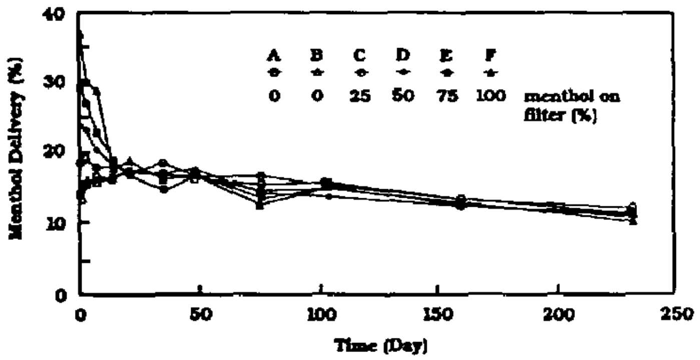


CA = 25 mm, 2.7/46,000; PAPER TUBE = 25 mm
POLYPROPYLENE = 25 mm, 4.5/32,000-38,500

THE EFFECTS OF MENTHOL PLACEMENT

In 1972, Curran reported that the age of mentholated products and the distribution of menthol between filter and tobacco can affect menthol transfer efficiencies (3). He found that 28 days after menthol application to filters, 41% of the menthol had migrated to the tobacco rod; and, that 28 days after application of menthol to tobacco, 20% had migrated to the filters. After completing migration and smoke studies with commercially available 85 mm cigarettes (65 mm rods and 20 mm filters plasticized with an undisclosed level of 55/45 triacetin/polyethylene glycol), he concluded that "menthol distribution between the tobacco and filter does not affect the amount of menthol delivered by individual puffs over the 95:5 to 80:20 (menthol tobacco:filter ratio) range but does affect it over the 30:70 to 59:41 range." Further, he concluded that for maximum menthol transfer efficiency, a mentholated cigarette with 70% of the menthol on the tobacco column and 30% on the filter might be more satisfactory than a cigarette which had menthol applied only to the tobacco. In 1979, Park *et al.* also found increased menthol transfers to MS as the menthol level on the filter increased (20). This was recently corroborated by Deutsch (7). In a study that had from 0% to 100% of the menthol applied to the filters in 25% increments, he found that application of 25% to 50% of the menthol to the filters minimized changes in menthol transfer with time as shown in Figure 3. Deutsch found highest 0-time transfer when 100% of the menthol was on the filter, but transfer began decreasing immediately.

FIG. 3
Percent Delivery Of Applied Menthol
(Data From Deutsch, 1990, Reference 7)



Also, Curran found no difference in the rate of menthol transfer to MS (about 19%) from filtered cigarettes with menthol applied to the tobacco after 3 and 28 days of aging (3). However, for cigarettes with menthol added to the filters, the MS transfer was 49% after 3 days and 31% after 28 days of aging (see Table V). This illustrates that there are effects of age and location of menthol application on menthol transfer to MS from cigarettes with plasticized filters.

TABLE V

The Effects Of Cigarette Age And Menthol Placement
On Menthol Delivery
(Data From Curran, 1972, Reference 3)

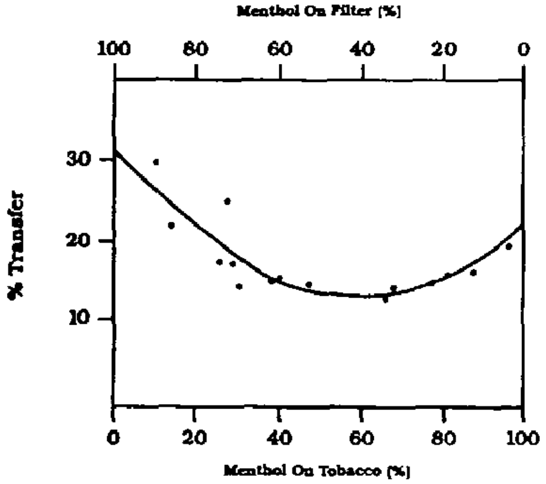
	Menthol Transfers			
	Cigarette F		Cigarette T	
Age (Days)	(mg)	(%)	(mg)	(%)
3	0.92	49	0.48	20
28	0.59	31	0.45	19

Cigarette F = All menthol applied to filter
Cigarette T = All menthol applied to tobacco

The influence of application site on menthol transfer to MS was also studied by Brozinski *et al.* (2) and Eble (9).

In 1973, Riehl *et al.* reported on menthol migration and transfer to MS for 84 mm cigarettes prepared with 21 mm filters (25). Plasticizer levels on the filters were not reported. When menthol was applied to the filters, 40% migrated to the tobacco after four weeks aging. When all of the menthol was applied to the tobacco, 30% migrated to the filters. Like Curran and Deutsch, Riehl *et al.* also found the highest menthol transfer to MS when most of the menthol was on the filters (see Figure 4). It is important to note that the age of cigarettes when smoked was not given. The importance of age, already suggested by Curran, will become even more apparent later in this paper.

FIG. 4
Menthol Transfer To Smoke From
Different Menthol Distributions
(Data From Riehl et al., 1973, Reference 25)



EFFECTS OF LIQUID FILTER ADDITIVES

In 1975, Curran reported the effects of liquid filter additives on menthol migration from tobacco to filters and delivery to MS after six weeks aging (4). He used experimental cigarettes constructed from purchased 64 mm tobacco rods fitted with 3.3/39,000 CA tow filters with a menthol content of 2.0 ± 0.1 mg. He found limited menthol migration to filters without triacetin (10% after six weeks) and that menthol migration increased with increasing plasticizer level (24% and 32% migration after six weeks aging for 5% and 8% triacetin levels, respectively). It was found that menthol transfer to MS was greater for filters containing 5% triacetin as compared to filters with 0% and 8% triacetin (see Table VI). Addition of 1,2-propanediol (propylene glycol) to plasticized filters resulted in increased menthol migration while glycerol addition had no effect.

Nevertheless, addition of either 1,2-propanediol or glycerol to the filter resulted in reduced menthol transfer to MS.

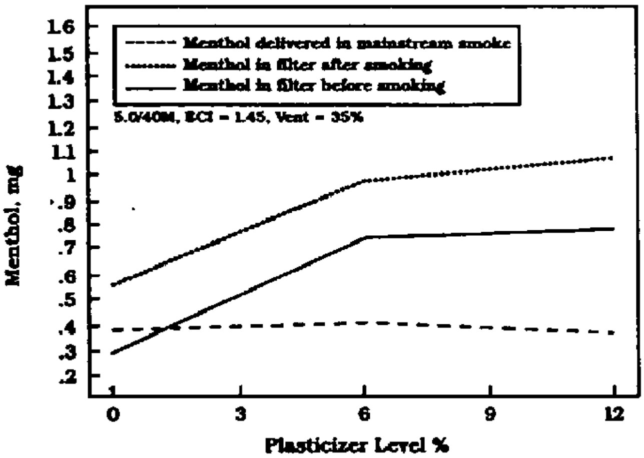
TABLE VI

Effect Of Filter Additives On Menthol Delivery And Migration
(Data From Curran, 1975, Reference 4)

Additive	Menthol Delivery (mg) 6 Weeks	Menthol Delivery (mg) 1,3,6 Week Average	Menthol On Filter At 6 Weeks
Control (0%)	0.32	0.34	10%
Triacetin (5%)	0.38	0.39	24%
Triacetin (8%)	0.36	0.36	32%
Triethylene Glycol Diacetate (5%)	0.31	0.33	28%
Triethylene Glycol Diacetate (8%)	0.27	0.30	34%
Control (0%)	0.36	0.36	31%
Glycerol (6%)	0.27	0.30	31%
Glycerol (10%)	0.27	0.30	31%
1,2-Propanediol (6%)	0.27	0.29	42%
1,2-Propanediol (10%)	0.22	0.27	42%

Data collected by Lewis and Norman indicated that for maximum menthol yield from CA filters the maximum triacetin level should be below 8% (13). They conducted studies to determine the effects of plasticizer level on menthol level measured on filters before and after smoking and on the level of menthol transferred to MS. For cigarettes that were aged three weeks, it was found that the actual MS menthol level increased slightly for 6% plasticizer application on the filter (0.41 milligram per cigarette) compared to the 0% and 12% plasticizer levels, both of which transferred 0.38 milligram per cigarette (see Figure 5).

FIG. 5
Effect Of Plasticizer On MS Menthol
Yield And Filter Deposition
(Data From Lewis And Norman, 1985, Reference 13)

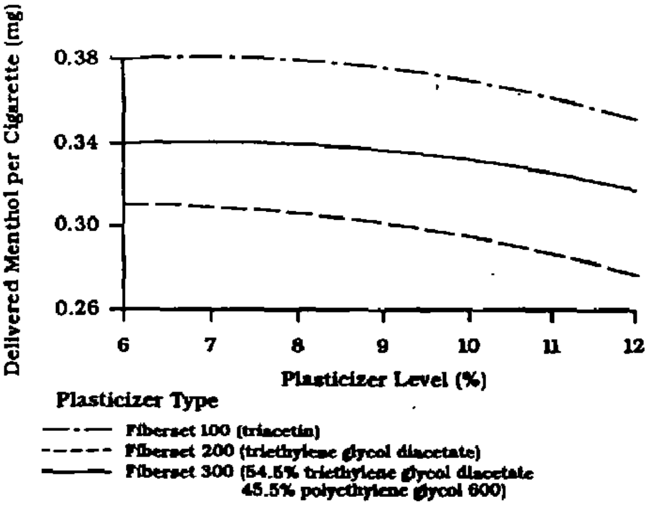


ECI = effective crimp index
Vent = % filter ventilation

These data agree with the findings of Woods (32) that MS menthol yields decreased as the filter plasticizer level increased from 6% to 12% (see Figure 6). Woods did not report results on lower plasticizer levels. Data from Woods' study indicate that MS menthol yield is influenced by plasticizer type, with more efficient transfer from filters plasticized with triacetin. Data from both studies illustrate that menthol yield is influenced by plasticizer level. Lewis and Norman also found that the menthol level measured in the filter after smoking was higher at each triacetin level than before smoking. For smoked and unsmoked filters, filter menthol level increased significantly with plasticizer applications of 0% to 6% and then remained fairly constant up to 12% plasticizer application (see Figure 5). Lewis and

Norman used 84 mm long cigarettes that were made with 27 mm on-line laser perforated CA filters.

FIG. 6
Effect Of Plasticizer Type And Level
On Delivered Menthol Per Cigarette
(Data From Woods, 1983, Reference 32)

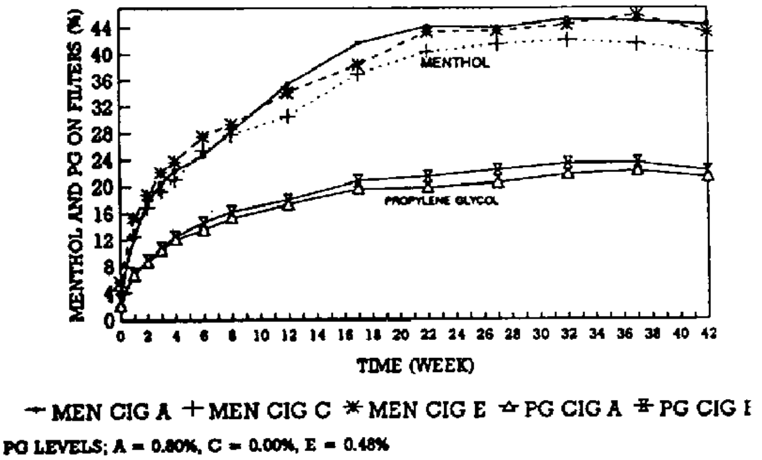


In a 1990 study to provide a mechanistic description of menthol delivery, Renfro reported effects of the absence and presence of triacetin in CA filters (4). He found that menthol migrated faster to filters plasticized with triacetin. This was in agreement with previously published studies (4, 6). Also, he reported that menthol eluted more efficiently from a filter made without triacetin. He concluded that, even with filters treated with triacetin, menthol in the filter is about twice as likely to be delivered to the MS as is menthol in the tobacco column.

EFFECT OF BLEND PROPYLENE GLYCOL ON MENTHOL TRANSFER

Since propylene glycol is extremely volatile, the effect of propylene glycol on menthol migration to filters seen by Curran was not unexpected. Results from a study in our laboratories to determine the effects of propylene glycol on menthol migration within the cigarette and its effect on menthol transfer to MS (1) show that propylene glycol migrates from the tobacco rod to filter at about one-half the rate of menthol migration (see Figure 7).

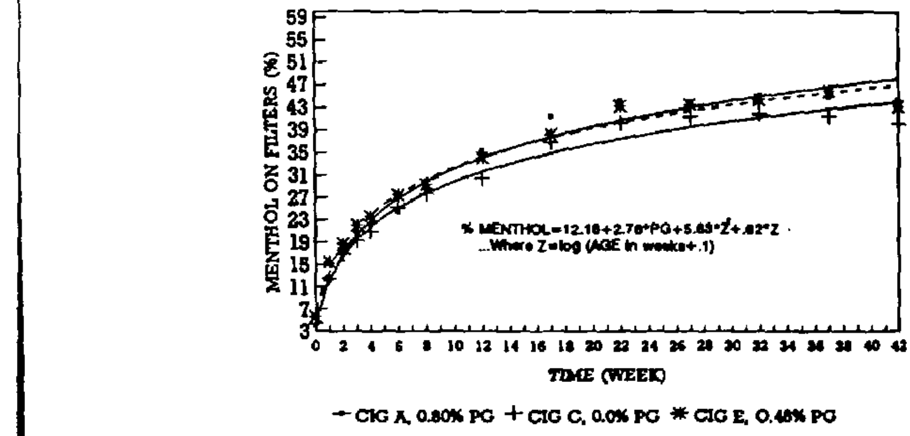
FIG. 7
Menthol And Propylene Glycol (PG) Migration Over Time To Filters Of Cigarettes With Different PG Levels
(Data From Best, 1992, Reference 1)



Cigarette A was a popular brand with 0.8% propylene glycol, Cigarette E was identical to Cigarette A except the propylene glycol level was 0.48% and Cigarette C required slight blend changes to eliminate all propylene glycol sources and to achieve a 0% propylene glycol level. All three products had identical CA filters treated with 7% triacetin.

Since menthol is very soluble in propylene glycol and in many cases there is more propylene glycol than menthol in mentholated cigarettes, it seemed very likely that propylene glycol would influence menthol migration and transfer to MS. After 42 weeks aging of cigarettes with identical filters and menthol applications, 40% of the menthol migrated to the filter of product C made with no propylene glycol and 43% and 44% to filters of products A and E with 0.48% and 0.80% propylene glycol, respectively. Regression analysis (14) of these migration data found that product C with no propylene glycol product had an intercept about 2.78% lower than the intercepts for products with propylene glycol, A and E (see Figure 8).

FIG. 8
Effect Of Propylene Glycol (PG) Application Rate On Menthol Migration To The Filter*
(Data From Mangan, 1992, Reference 14)

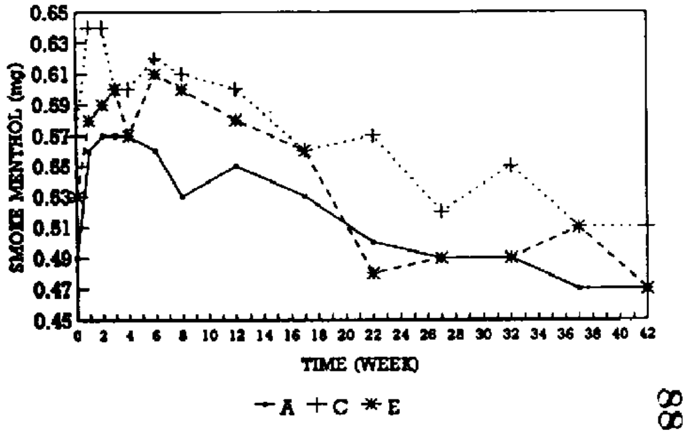


* = Log regression plot

The regression equations for the products made with propylene glycol are not distinguishable from each other but are consistently different from the regression equation for the product made without propylene glycol. Therefore, the differences in menthol migration rates for products made with and without propylene glycol are statistically significant. Absence of propylene glycol in the blend, as well as in the filter as noted previously by Curran (4), results in reduced menthol migration to filters.

It was further speculated that propylene glycol levels in the blend and its consequent migration to the filter should have an effect on menthol transfer to MS. Curran reported earlier that propylene glycol added to the filter influenced menthol transfer to MS. Evaluation of menthol MS yields for the three filtered products studied in our laboratories with different levels of propylene glycol applied to the blend indicates that propylene glycol levels influence menthol transfer to MS (see Figure 9). Small but statistically significant differences were observed.

FIG. 9
Smoke Menthol Yield Over Time From Filtered Cigarettes
(Data From Best, 1992, Reference 1)



PROPYLENE GLYCOL A = 0.80%, C = 0.0%, E = 0.48%

The average menthol transfer over 42 weeks was 17.49% ± 1.01% and 17.88% ± 0.99% for products A and E, respectively. The transfer rate of 19.05% ± 0.75% for product C indicated a more efficient menthol transfer rate to MS smoke. Each data point plotted in Figure 9 represents an average of four replicates. It is interesting to note that the MS menthol transfer pattern for each product does not represent a smooth line, but rather a cycling phenomenon. This phenomenon will be discussed later in this paper. Although significant differences in menthol transfer efficiencies were determined for products made with and without propylene glycol, the results of Perfetti's and Gordin's menthol JND study (22) suggest that menthol related perceptual differences do not exist. JND studies are used to determine the change in stimulus doses (in this case MS menthol) necessary to be detected as different (sensorially) by a specific proportion of a population. For example, JND_{50} connotes that 50% of a population could detect a menthol sensory change at some level of smoke menthol difference compared to a reference product. Earlier work by Curran (3) showed the effect of age and filter additives on menthol migration and transfer in filtered cigarettes. In this study, the effect of a blend additive was illustrated.

EFFECTS OF AGING

In 1972, Brozinski *et al.* reported the effects of age and initial menthol placement on menthol migration and transfer to smoke (2). They applied menthol to tobacco and to filters and determined migration rates in both directions as a function of time. They also determined menthol transfer to smoke from eight commercially available mentholated U. S. and German cigarettes. Some of the cigarettes were 85 mm and some were 100 mm in length. The filter lengths (18 mm to 25 mm), weights (120 mg to 125 mg), resistance to draw (53 mm to 75 mm H_2O) and nicotine filtering efficiencies varied. The cigarettes contained between 0.125 mg and 3.19 mg of total menthol with 25% to 42% on the filters at time of smoking. The authors concluded that there was no major effect of menthol application level on migration rates. Although cigarette age at smoking was not reported (probably between 2 and 5 months old), menthol MS transfer efficiencies of 28% to 42% were measured (see Table VII).

TABLE VII

Comparative Analysis Of Cigarette Brands
(Data From Brozinski *et al.*, 1972, Reference 2)

	Menthol			Smoke Menthol	
Cigarette	Rod (mg)	Filter (mg)	Cigarette (mg/cig)	Smoke (mg/cig)	Transfer (%)
A	2.11	1.08	3.19	1.12	35
B	1.95	0.86	2.81	0.88	31
C	1.58	0.77	2.35	0.76	32
D	1.70	0.57	2.27	0.64	28
E	1.29	0.77	2.05	0.76	37
F	1.13	0.83	1.95	0.81	42
G	1.00	0.56	1.56	0.52	33
H	0.079	0.046	0.125	0.035	28

Although specific cigarette construction parameters were not reported, Brozinski *et al.* found identical menthol MS transfer efficiencies of 28% for cigarettes with total menthol loads of 0.125 mg and 2.27 mg per cigarette. These data indicate that there was no major effect of menthol application level on transfer efficiency. In an aging study (2), Brozinski found that menthol transfer to MS increased from 0-time to one month, after which it leveled off through five months and then decreased through nine months (see Table VIII). This is the trend that is generally observed for filtered cigarettes when all of the menthol is applied to the tobacco.

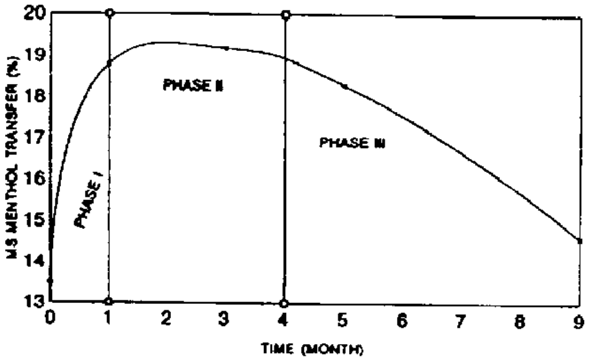
TABLE VIII

Menthol Transfer To Smoke; An Aging Study
(Data From Brozinski *et al.*, 1972, Reference 2)

Time (Months)	Menthol		Menthol Transfer To MS Smoke	
	Filter (%)	Cigarette (mg)	mg/cig	(%)
0	0.7	2.88	0.39	13.5
1	20.9	2.34	0.44	18.8
3	29.9	2.71	0.52	19.2
5	35.5	2.62	0.48	18.3
9	41.8	2.94	0.43	14.6

Perfetti drew some profound conclusions from the work of Brozinski *et al.* as well as from several other studies dealing with menthol migration, transfer and filter retention data (21). Three different phases in the expected shelf life of mentholated cigarettes were proposed as illustrated in Figure 10. During Phase I, the freshly prepared cigarette has essentially no menthol on its filter and thus initially tranfers smaller amounts of menthol to MS because of its high filter efficiency for menthol. Later in Phase I, menthol very rapidly migrates to the filter and effectively decreases the cigarette filtering efficiency for menthol which results in greater transfers to MS. Phase II begins when the efficiency of the filter for menthol remains relatively constant; that is, when elution from the filter and removal from MS are roughly equal. This occurs over a fairly large range (20% to 35% in filter). Migration of menthol to the filter continues until equilibrium is reached (generally, 45% to 50% on the filters and 50% to 55% on the tobacco of blended cigarettes). As the length of storage time increases, there is eventually a decrease in the amount of menthol in the MS. This is Phase III. During this period, menthol is believed to be more deeply sorbed into the filter fibers and thus may not be available for elution. Mathis found that penetration into plasticized CA filters, over time, resulted in reduced transfers to MS for a series of filter flavors (15) thereby indicating that this process is not unique to menthol.

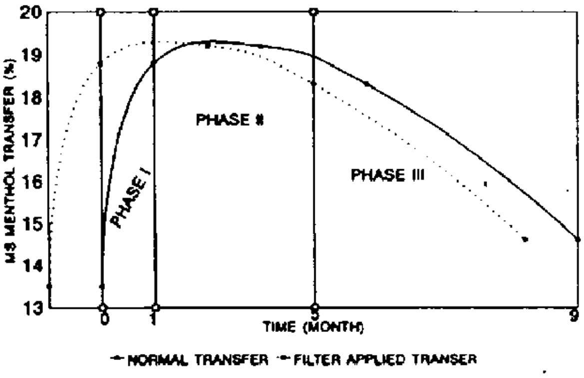
FIG. 10
Proposed Theory Of Menthol Migration/Transfer
For Conventional* Filtered Menthol Cigarettes
(Data From Perfetti, 1985, Reference 21 And
Brozinski *et al.*, 1972, Reference 2)



* Menthol applied to tobacco blend

Preloading filters with menthol eliminates or greatly reduces the effects of Phase I by shifting the transfer profile to the left as shown in Figure 11 (21). Projected menthol yields from cigarettes with preloaded filters are expected to provide more efficient menthol transfers at 0-time much like an unfiltered cigarette. However, Phase III will occur at a much earlier cigarette age to decrease menthol MS yields. With 84 mm cigarettes constructed with 21 mm standard CA tow filters bonded with 6% triacetin, as noted earlier, Deutsch found that MS menthol transfers increased at 0-time as the level of menthol applied to the filter was increased as shown in Figure 3, and that after a few weeks, transfers were equivalent regardless of application site (7).

FIG. 11
Proposed Theory Of Menthol Migration/Transfer For Filtered Cigarettes With Menthol* Applied To Filter
(Data From Perfetti, 1985, Reference 21)

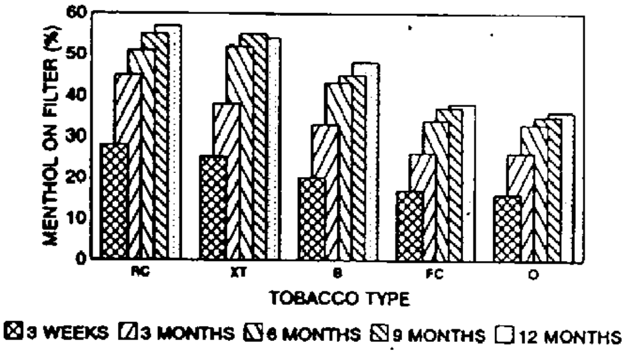


* Only a portion of the menthol was applied to the filter

EFFECTS OF TOBACCO TYPE

The influence of tobacco type on menthol migration and transfer to MS has been investigated in our laboratories (31). Wong *et al.* made single tobacco cigarettes from burley (B), flue-cured Virginia (FC), oriental (O), reconstituted sheet (RC) and a blend of expanded burley and Virginia (XT) tobaccos. Cigarettes were fitted with identical CA undiluted filters made from 2.7/39,000 tow and treated with 7.19% triacetin. Menthol (about 0.45% pack menthol) was applied via top dressing to each tobacco type. Menthol migration to the filter and transfer to MS were measured at three weeks, three months, six months, nine months and 12 months. There were large differences in migration rates for the different tobacco types (see Figure 12). After one year, they found 57%, 54%, 48%, 38% and 36% of the menthol migrated to the filters of RC, XT, B, FC and O products, respectively. There were comparable differences at each sampling time point. Since the filters were identical, these data suggest the following order of menthol affinity for different blend components: O > FC > B > XT > RC. Note, in Figure 12, that even after one year, menthol migration appeared to level off only for the XT product and was still occurring in the other products.

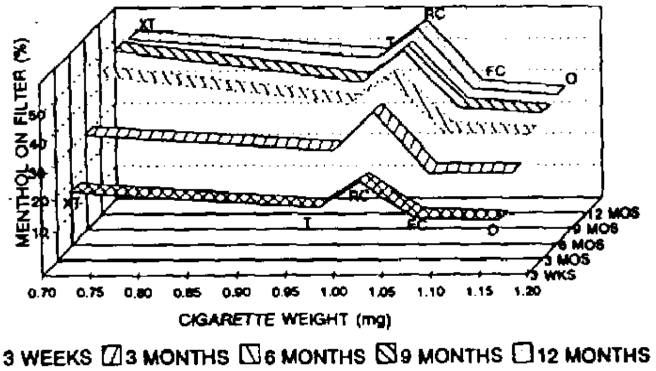
FIG. 12
Menthol Migration From Tobacco Rod To Filter
From Different Tobacco Types Over Time
(Data From Wong et al., 1988, Reference 31)



RC = Reconstituted sheet; XT = Expanded tobacco;
B = Burley; FC = Flue-cured; O = Oriental

Because of differing tobacco densities, these products were made to a tobacco rod firmness target and as such contain different amounts of tobacco due to the difference in the rod filling capacity for the different tobacco types. When menthol migration to the filter was plotted versus tobacco weight, low affinity for menthol in the RC product was readily apparent (see Figure 13). Percent pack menthol (total amount of menthol on rods and filters) values were relatively stable over the 12 month period for all products except the RC product which experienced a 15% drop. This drop was due to its low affinity for menthol. The significance of this drop will be discussed later in this report. While many studies have suggested that mentholated cigarettes equilibrate over time, such that about 50% of the menthol is in the plasticized CA filter regardless of original application site, these data suggest that this may only be true for a blended cigarette since different tobacco types have different affinities for menthol.

FIG. 13
Menthol Migration From Rod To Filter
From Different Tobacco Types
(Data From Wong et al., 1985, Reference 31)

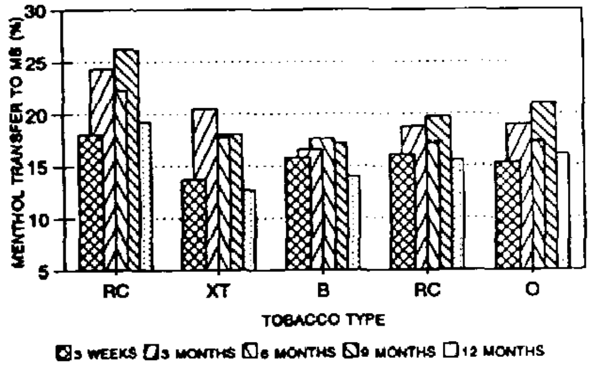


RC = Reconstituted sheet; XT = Expanded tobacco;
B= Burley; FC = Flue-cured; O = Oriental

In this single tobacco type study, the transfer of menthol to MS from the individual tobacco types was similar to trends seen in the past for blended filter cigarettes. Over time, transfer of menthol to MS increased for about six months and then decreased (see Figure 14). Absolute transfer of menthol is influenced by application level and changes in pack menthol (available menthol). On a percentage basis, increases in menthol transfers to MS are usually coupled with decreases in menthol transfers to SS and vice versa. The MS/SS distribution is predominantly a function of the burn rate, or more specifically, the amount of tobacco consumed during puff and smolder periods. As more tobacco is consumed during puffing, transfer to MS increases and transfer to SS decreases. These MS/SS distributions can be controlled by cigarette construction parameters or by altering puffing frequency and/or volume. However, the burn rates of different tobacco types are inherently different. Since burn rates were not measured in this study, the only way to assess the impact of burn rate was by analysis of puff count (number of puffs required to consume the same length of tobacco rod). Menthol transfers to MS very efficiently from freshly mentholated filters whether application is intentional or by migration. As noted earlier, after menthol migrates to a plasticized CA filter, it begins to penetrate the fibers making less menthol available for elution. As long as migration exceeds penetration, menthol transfer to MS increases. Once equilibration is achieved, menthol penetration into the CA fibers continues and MS transfer drops. As expected, MS transfers increase to a point with increased menthol level on the filter. This is illustrated in Figure 12 and Figure 14.

FIG. 14

Smoke Menthol Transfer For Different Tobacco Types Over Time (Data From Wong et al., 1988, Reference 31)



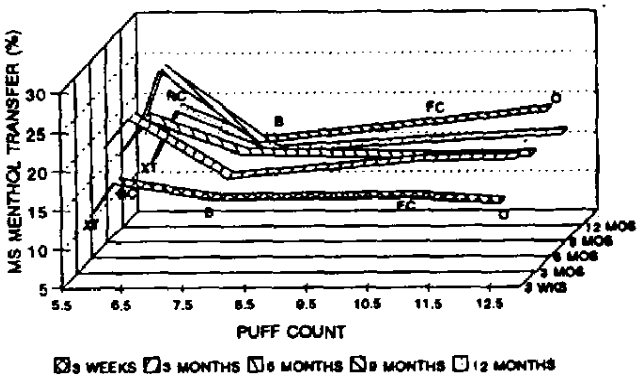
XT = Expanded tobacco, RC = Reconstituted sheet,
B = Burley, FC = Flue-cured, O = Oriental

When percent MS menthol transfer is plotted versus puff count, as illustrated in Figure 15, based on the migration data, MS menthol transfer was expected to occur in the following order: RC > XT > B > FC > O. The RC product exhibited most efficient MS menthol transfer; however, transfer trends from the other components were just the opposite of what was expected, with O > FC > B > XT. This suggests that lower MS transfer rates are due to greater consumption of tobacco during smolder resulting in more menthol transfer to SS. As expected, the highly processed RC material had very little affinity for menthol and exhibited high menthol migration to the filters which resulted in higher transfer to MS.

FIG. 15

Smoke Menthol Transfer From Different Tobacco Types

(Data From Wong *et al.*, 1988, Reference 31)



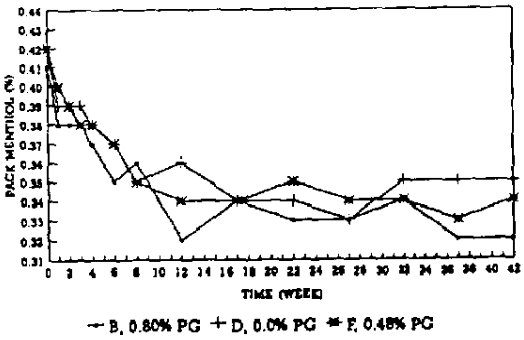
XT = Expanded tobacco; RC = Reconstituted sheet;
B = Burley; FC = Flue-cured; O = Oriental

EFFECTS OF PACKAGING

As noted earlier in the single tobacco type study, pack menthol of the reconstituted tobacco product decreased over time indicating very low menthol affinity for this particular smoking material. There is competition between blended tobacco rods and plasticized CA filters for the available menthol. Both have tremendous menthol affinities. Brozinski *et al.* found a distribution coefficient of approximately 4.5 (plasticized filter:tobacco rod) at equilibrium (2). This coefficient would be expected to vary with different plasticizer levels. Dube found levels of 2% and 5% menthol migration from conventional blended filtered cigarettes to soft pack and crush proof boxes (CPB's), respectively (8). The menthol levels of these packaging materials are in good agreement with those found by Renfro (24). In the study discussed previously to investigate the effect of propylene glycol on menthol migration and transfer with filtered cigarettes, the effect of propylene glycol on the transfer to MS from unfiltered cigarettes was also investigated (1). Tobacco rods and menthol content of products B, D and F, were identical to the previously described filtered products, A, C and E, respectively. All products had approximately 0.42% menthol applied to the tobacco blend. Products B, D and F were prepared with cardboard mouthpieces instead of CA filters. With use of the cardboard mouthpieces, unfiltered cigarettes were smoked to the same butt length as the filtered cigarettes and consumed the same amount of tobacco and menthol. Pack menthol levels decreased through about 8 to 12 weeks (see Figure 16). These pack menthol decreases were accompanied by reduced MS menthol yield (see Figure 17). Packaging material permeability was assumed to be the cause until it was observed that the percent pack menthol values and MS transfer levels remained fairly constant for the rest of the 42 week study. This eliminated the permeability theory. Another logical explanation was migration of menthol to packaging material resulting in reduced amounts of menthol available for transfer to MS (see Table IX). The data supported this hypothesis. In the absence of the tremendous menthol affinity provided by a plasticized CA filter, significant menthol migration to packaging materials occurred until the packaging materials were saturated. As much as 19%

of the applied menthol was found on the CPB. When the menthol found on the packaging materials was added to that in the cigarette, a menthol material balance was achieved.

FIG. 16
Pack Menthol: Unfiltered* Cigarettes Over 42 Weeks
(Data From Best, 1992, Reference 1)



* HAD CARDBOARD MOUTHPIECES

FIG. 17
MS Menthol Yields From Unfiltered Cigarettes
(Data From Best, 1992, Reference 1)

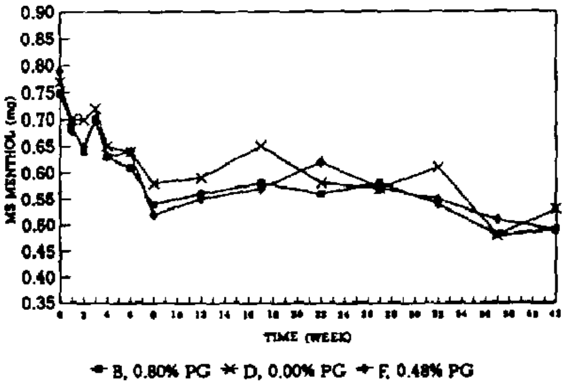


TABLE IX

Menthol Migration To CPB Packaging Material Of Unfiltered KS Cigarette With Cardboard Mouthpieces
(Data From Best, 1992, Reference 1)

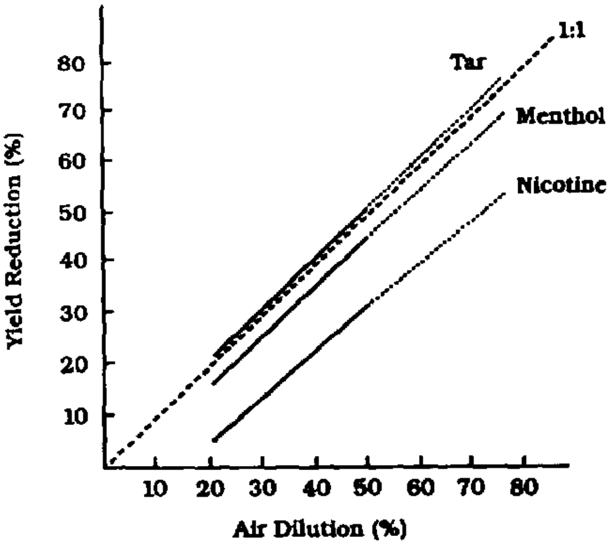
	Time (Weeks)			
	0	8	17	55
% Pack Menthol	0.41	0.36	0.34	0.33
Menthol (mg):				
Rod	2.94	2.27	2.24	2.33**
Mouthpiece	0.07	0.27	0.25	
Outerwrap*	0.00	0.038	0.045	0.043
Crushproof Box	0.00	0.409	0.529	0.564
Cigarette	3.01	2.99	3.06	2.94
% Menthol On CPB	0	13	17	19

*Adjusted to milligrams per cigarette
**Rod and mouthpiece

EFFECTS OF CIGARETTE CONSTRUCTION PARAMETERS

In 1982, Shofner and Ireland investigated the effect of air dilution on 'tar', menthol and nicotine transfer (27). They observed that percent yield reductions were linear for all three parameters over a 20% to 50% dilution range (see Figure 18). They found, that, "As expected, the yield reduction of smoke condensate approached the 1:1 ratio line when compared to air dilution. On a percent reduction basis, menthol reduced more than nicotine. Increasing air dilution reduced the amount of smoke condensate delivered but had less of an effect on menthol and nicotine. The efficiency at which menthol and nicotine are transferred into mainstream particulate increases even though less particulate smoke is delivered. Therefore, by increasing air dilution, the nicotine to 'tar' ratio of smoke condensate was increased more than the menthol to 'tar' ratio." For ventilation levels of 20% to 50%, air dilution had a smaller effect on reducing menthol yields compared to particulate matter yields and had an even smaller effect on nicotine percent reductions.

FIG. 18
The Effect Of Air Dilution On Percent Yield Reduction
For 'Tar', Nicotine And Menthol
(Data from Shofner and Ireland, 1982, Reference 27)



In 1983, Woods reported on effects of CA filter and fiber parameters on menthol migration and transfer (32). Woods found that at a given time after cigarette preparation, the level of menthol found on filters increased with increasing plasticizer level. This supported the earlier findings of Curran (4). Woods further reported that menthol yields per cigarette decreased with increased plasticizer level. The parameters investigated by Woods are listed in Table X in order of the impact of their effects on MS menthol yields.

TABLE X

Filter And Fiber Parameter Effects On Delivered Menthol In Order Of Significance
(Data From Woods, 1983, Reference 32)

Plasticizer Type

Total Denier

Plasticizer Level

Denier Per Filament

Results and cigarette descriptions from a study by Curran (5) to determine the effect of filter surface area, filter weight, plasticizers, plasticizer concentration and storage time on menthol migration from the tobacco to an acetate filter of a filter cigarette are compiled in Table XI. Curran reported that, although there were significant differences in the menthol content of filters with three different surface areas (171, 229 and 382 cm^2), there was no correlation between filter surface area and the percentage of menthol that migrated from the tobacco to the filter. His data show that, at constant total denier, menthol migration is faster at the higher surface area/lower denier per filament (dpf) condition. Curran purchased 84 mm cigarettes, removed the filters and replaced them with unmentholated experimental filters that were plasticized with 6% triacetin unless otherwise noted. Where dpf, total denier and plasticizer level were constant, a 10% increase in filter weight (142 mg to 156 mg) resulted in only a 4% to 5% increase (21.7% to 22.7%) in menthol migration. He also saw a definite effect of plasticizer level on menthol migration. Lewis and Norman (13) found that as dpf increased (i.e., as fewer fibers were incorporated into the tow bundle), surface area available for menthol sorption decreased and the amount of menthol available for delivery to mainstream was increased.

TABLE XI

Effect Of Filter Surface Area, Weight, Plasticizer, Plasticizer Concentration And Storage Time On Menthol Migration

(Data From Curran, Reference 5)

DPP*	Total Denier	Surface Area (cm^2)	% PZ**	% Menthol On Filter Storage Time (Days)						
				0	4	9	14	22	28	54
8.0	80,000	171	6	-	5.4	6.6	6.9	9.7	14.5	23.7
5.0	80,000	229	6	-	5.4	8.6	8.2	11.1	17.8	27.9
1.6	57,000	382	6	-	5.3	8.3	8.2	10.4	17.0	26.6
		Filter Weight (mg)								
3.3	42,000	142	6	-	4.5	5.7	7.0	8.7	15.0	21.7
3.3	42,000	156	6	-	4.5	5.7	8.0	10.3	15.7	22.7
3.3	42,000	-	0	0	-	0.0	0.0	0.0	0.2	0.7
3.3	42,000	-	4	0	-	4.8	6.4	6.5	10.7	12.0
3.3	42,000	-	8	0	-	6.5	11.3	11.7	14.7	21.9

*DPF = Denier per filament

** PZ = Plasticizer

Effects of some filter tow parameters on menthol migration and transfer to MS are well explained in Hoechst Celanese Technical Bulletin FPB-11 (10). Using 84 mm cigarettes with 27 mm CA tow tips treated with 9% triacetin, menthol migrated more efficiently to filters of higher total denier (see Figure 19). When dpf and pressure drop were held constant, the effect was attributable to mass differences. When calculated on an equal weight basis, menthol migration was equivalent for total denier levels. When pressure drop and total denier were held constant, menthol migration to the filter increased with increasing dpf due to the greater tow weight required to achieve a constant pressure drop (see Figure 20).

FIG. 19
Effect Of Total Denier On Tip Menthol Gain During Storage
(Data From Hoechst Celanese Technical Bulletin, 1992,
Reference 10)

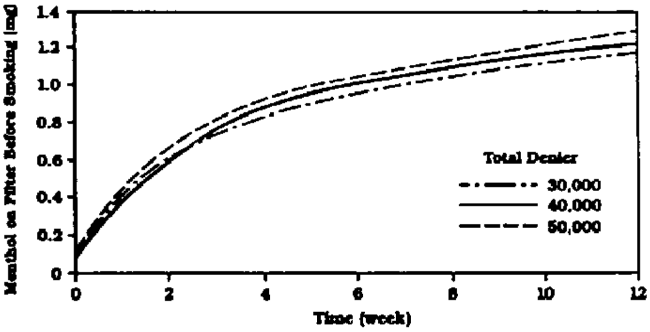
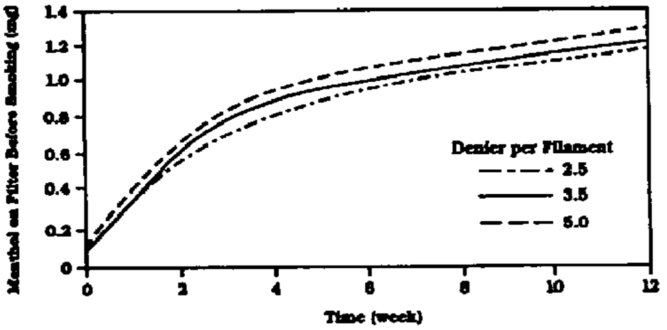


FIG. 20
Effect Of Tow DPF On Tip Menthol Absorption During Storage
(Data From Hoechst Celanese Technical Bulletin, 1992,
Reference 10)



Effect of total denier on menthol transfer to MS (over the 12 week storage period) is shown in Figure 21. As total denier increases, MS menthol yields decrease. This is due to greater menthol absorption (result of higher surface area) at higher total denier. As illustrated in Figure 22, menthol transfer to MS was not affected by denier per filament.

FIG. 21
Effect Of Total Denier On Delivered Menthol
(Data From Hoechst Celanese Technical Bulletin, 1992, Reference 10)

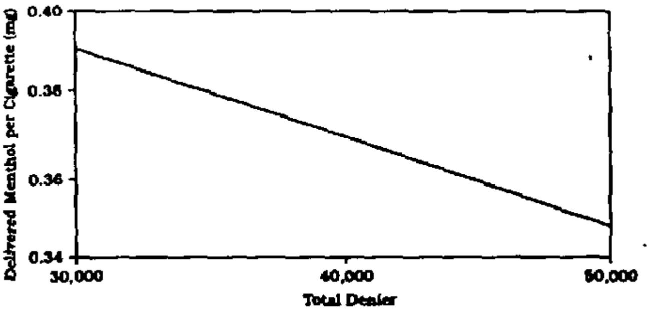
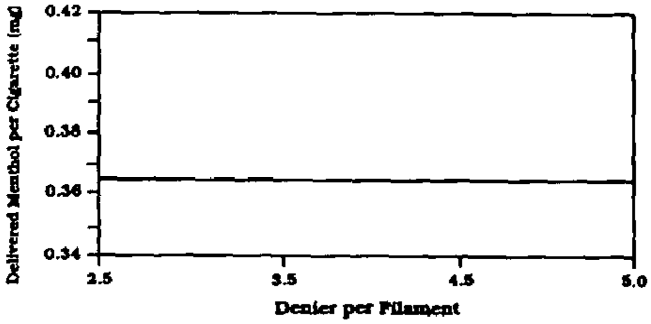
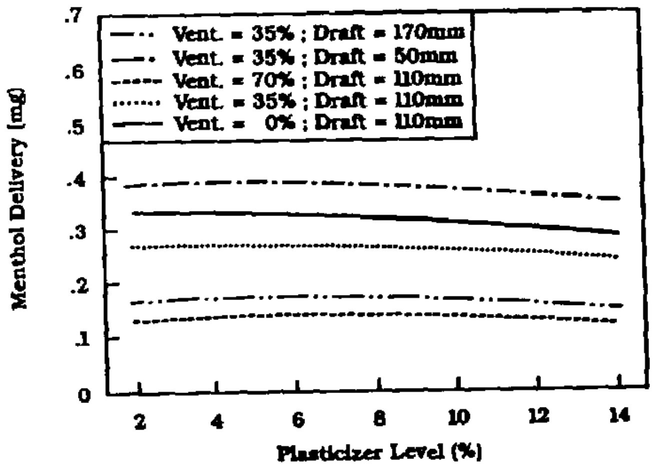


FIG. 22
Effect Of Tow DPF On Delivered Menthol
(Data From Hoechst Celanese Technical Bulletin, 1992, Reference 10)



In the early 1980's, Norman *et al.* studied the effect of filter pressure drop (varied by changing tow items), filter ventilation level (obtained by on-line laser perforation), filter plasticizer (triacetin) level and tobacco menthol load on MS menthol yields of a popular 84 mm cigarette made with a 27 mm filter (18). They developed regression models of MS yields as functions of the four variables. The scope of this presentation does not include the model development but some of the results of the study will be discussed. Figure 23 thru Figure 26 and Figure 28 were calculated from the regression models. MS menthol yields were significantly correlated with filter draft, ventilation level and tobacco menthol load. A small but statistically significant regression coefficient was also found for the plasticizer level. At given plasticizer and filter draft levels, as ventilation level increased, menthol yields decreased (see Figure 23). Also, at given plasticizer and filter ventilation levels, as filter draft increased, menthol yields decreased. As plasticizer level increased there were slight decreases in menthol yields at all combinations. Therefore, menthol delivery at a given FTC 'tar' yield depends on the particular combination of filter draft and ventilation level used. MS FTC 'tar' versus menthol yield is shown in Figure 24 for all three filter ventilation levels. Filter draft was varied to effect the changes in FTC 'tar'. As 'tar' increased, MS menthol yields increased at all ventilation levels. But, as ventilation levels increased, menthol increases were greater (in other words as 'tar' levels increased, menthol/'tar' ratios increased with increasing ventilation). Whitton and McAdam later reported a similar relationship between smoke yield and MS menthol transfer for an undiluted flue-cured cigarette (30). Norman *et al.* also investigated the effects of filter ventilation and draft on menthol transfer as illustrated in Figure 25. As ventilation increased, menthol transfer decreased for all three draft levels, and as draft increased, menthol transfer decreased. This relationship between menthol/'tar' ratios (µg/mg) and ventilation for different filter draft levels is shown in Figure 26.

FIG. 23
Computed Menthol Delivery As A Function
Of Plasticizer Level
(Data From Norman et al., 1984, Reference 18)



Draft units are mm H_2O at 17.5 cc/sec flow
Vent = filter ventilation

At lower draft levels the menthol per unit 'tar' increases with ventilation. At the higher draft level (170 mm) almost no effect of ventilation is observed. In the previously mentioned menthol JND study (22), it was found that tobacco menthol load (pack menthol) was most important to menthol delivery per unit 'tar'. Perfetti and Gordin found that for a particular configuration, the relationship between pack menthol (menthol load) and menthol transfer was highly linear for full flavor menthol (FFM), full flavor low 'tar' menthol (FFLTM) and ultra low 'tar' menthol (ULTM) products as shown in Figure 27 for the FFM product. Data for the FFLTM and ULT configurations were very similar. Figure 28 is a plot of menthol transfer as a function of FTC 'tar' yield when filter drafts were varied to effect changes in 'tar'. Menthol transfer increased with increased 'tar' yields and increased ventilation level. However, for a given 'tar' level, menthol transfer can be slightly increased by the combination of lowered filter drafts and increased ventilation. Although they can be used to influence menthol transfer, adjustment of the cigarette parameters in this study did little to improve menthol transfer efficiency. The range of control of menthol transfers was extremely limited when the 'tar' yield and tobacco menthol load were arbitrarily fixed.

FIG. 24
Computed Menthol Delivery As A Function Of FTC 'Tar'
(Data From Norman et al., 1984, Reference 18)

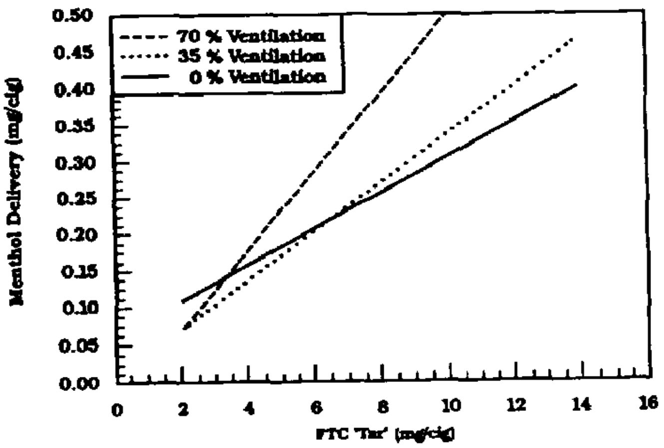
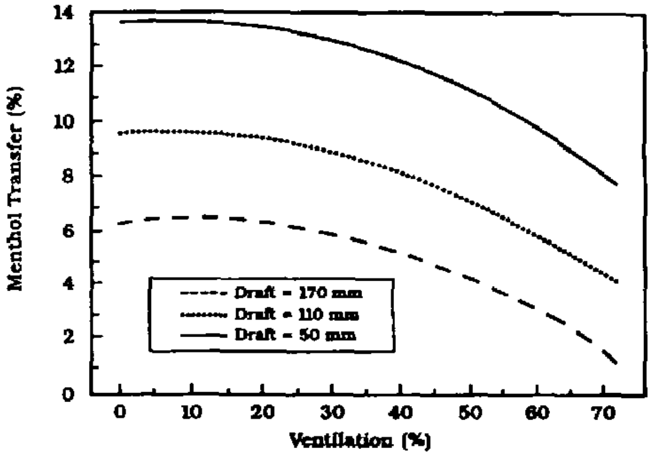


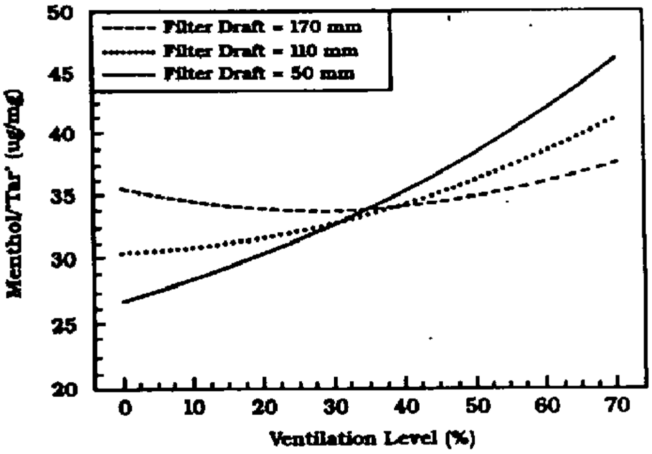
FIG. 25
Effects Of Ventilation And Filter Draft On
Fraction Of Applied Menthol Delivered
(Data From Norman et al., 1984, Reference 18)



Draft units are mm H_2O at 17.5 cc/sec flow

Whitton and McAdam described factors that influence menthol transfers from flue-cured tobacco cigarettes prepared with CA filters treated with 7% to 8% triacetin (30). They found that menthol transfer increased with increased smoke yield. They also found that menthol transfer is sensitive to chemical composition of smoke [Curran had claimed earlier that cigarette smoke changes the affinity of CA filters for menthol (4)]. They concluded that smoke moisture (over the range studied) had little influence on the amount of menthol transferred to smoke. Cigarette moisture content at time of smoking ranged from 5.1% to 12.8%. This is in good agreement with unpublished RJR findings (11, 18). When octanoic acid was added to the tobacco column, menthol transfer increased but was accompanied by a MS increase. In a study to measure menthol transfer from CA filters, Whitton and McAdam found that, because of high menthol levels in filters, filtration efficiency increased resulting in TPM decreases. Data in Table XII show the influence of menthol filter level on actual menthol transfer and transfer normalized to reflect TPM changes.

FIG. 26
Computed Menthol/'Tar' Ratios Versus
Ventilation Level For Various Filter Drafts
(Data From Norman et al., 1984, Reference 18)



Draft units are mm H_2O at 17.5 cc/sec flow

According to Whitton and McAdam, "these results indicate that the percent transfer levels are dependent upon the initial menthol loading on the filter, with higher transfer efficiency at low loading levels." The actual optimum menthol filter load is probably below 6.2%.

FIG. 27

Menthol JND For FF 85 mm Products

Pack Menthol Versus Smoke Menthol

(Data From Perfetti And Gordin, 1985, Reference 22)

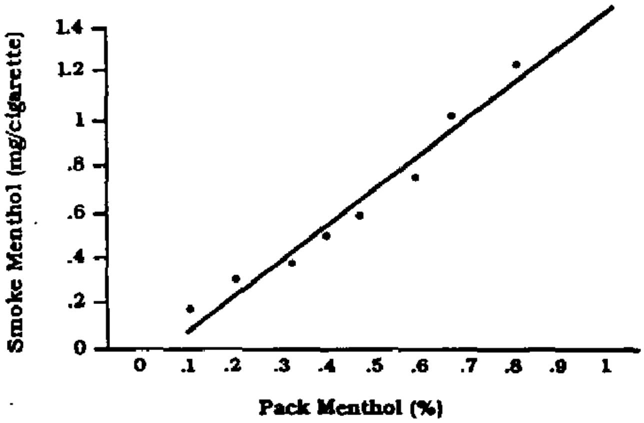


FIG. 28

Menthol Transfer As A Function Of FTC 'Tar' Delivery

As Varied By Ventilation And Filter Draft

(Data From Norman et al., 1984, Reference 18)

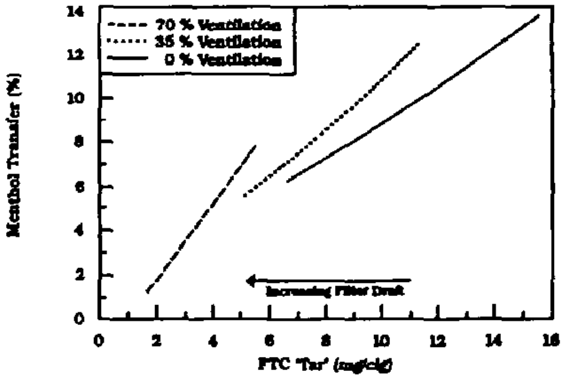


TABLE XII

Influence Of Load Level On Transfer Of Menthol From CA filters

(Data From Whitton, 1991, Reference 30)

	Menthol		
Filter Load (mg)	MS Yield (mg)	Actual Transfer (%)	Adjusted Transfer (%)
6.2	49.0	79	66
13.2	63.6	62	41
18.7	47.2	34	31
23.0	35.6	22	27
30.1	26.6	16	27
38.8	20.9	9	18

PATTERN OF MENTHOL TRANSFER TO MS OVER TIME

This presentation has dealt mainly with observations and some speculation about menthol migration and transfer. Some review and new disclosures have been included. One additional disclosure of an unusual phenomenon that has been observed in our laboratories over the last several years will be made in this presentation. Generally, menthol MS transfer patterns over time are illustrated as a smooth curve (see Figure 10). The menthol transfer pattern from filtered cigarettes to MS, increasing from 0-time to a peak at several weeks then gradually declining, was discussed earlier. However, close examination of the data in Figure 9 [each point is an average of 4 replicate analyses with very tight standard deviations (1)] show that menthol yield increased rapidly from 0-time levels for several weeks. However, following these initial increases, significant drops in menthol yield occurred followed by rises in menthol MS yields for all three products after peak yield was achieved. Menthol yield appears to cycle slightly throughout the study. These initial decreases in menthol yield occurred at different times: three weeks for the 0% propylene glycol product, four weeks for the 0.48% propylene glycol *product* and eight weeks for the 0.80% propylene glycol product, for these three different but very similar products, thus ruling out a time related analytical problem. Samples were submitted for analysis at the same time for all products at each time point. Similar menthol transfer patterns to MS, over time, have been noticed in the literature (7, 25, 28). These investigators, in the absence of statistical corroboration, made no assertion that these menthol transfer cycles were real. They may have felt that the random cycling in menthol yields was an analytical anomaly, and it may well be. However, for this study, menthol migration to filters was also measured for each set of cigarettes at the same time the MS menthol analyses were performed (see Figure 7) and there were no observed cycling phenomena in migration values. Examination of the results in light of the successful modeling studies on other cigarette behaviors (19, 29) has led to the following considerations:

a. Careful studies of changes in menthol transfer to MS with aging suggest a more complex behavior than previously reported.
b. There is evidence from these aging data that menthol transfers do not simply increase to a maximum then decline smoothly. Rather, there may be reproducible fine structure on the declining portion which is affected by various cigarette design parameters.
c. These results may be consistent with a more complex mechanism of menthol migration and transfer.
d. Detailed analysis of the kinetics of migration and menthol transfer to MS smoke with aging may give more insight into these details.

SUMMARY

As we have seen, menthol migration and transfer to MS with filtered cigarettes are complex processes. The following is an attempt to select some highlights from the old and new research:

a. Depending on cigarette construction parameters, over 50% of the menthol in a cigarette can be delivered to MS.

b. As a result of changes in contemporary cigarette construction to control the yield of total particulate matter, nicotine and other smoke components, menthol transfer to MS is generally 10% or less.

c. There is very little, 1% or less, menthol contribution to MS vapor phase as thermal decomposition products.

d. Cigarette construction parameters influence the distribution of menthol between MS and SS.

e. Menthol migrates rapidly to plasticized CA filters with plasticizer acting as the driving force.

f. Menthol on filters can both enhance and inhibit the transfer of menthol to MS.

g. When menthol is applied to the blend only, menthol transfer to smoke is low until about 20% of the menthol has migrated to the filters.

h. Menthol transfers to smoke very efficiently from freshly mentholated cigarette filters.

i. The optimum initial menthol level on the filter, for uniform menthol transfer to smoke over time, is 25% to 50%.

j. As menthol penetrates the fibers of plasticized CA filters over time, less is available for elution to MS and transfer efficiency decreases.

k. As long as menthol migration to the filter equals or exceeds penetration into the filter fibers, transfer efficiency to MS remains level or increases.

l. Propylene glycol added to filters enhances menthol migration to filters.

m. Addition of propylene glycol or glycerol to filters results in decreased menthol transfer to smoke.

n. Addition of propylene glycol to the blend results in propylene glycol migration to the filter which in turn enhances menthol migration to the filter.

However, this ultimately results in reduced menthol transfer to MS.

o. Different tobacco types have different affinities for menthol (oriental/Turkish > Virginia/flue-cured > burley > expanded burley/Virginia blend > reconstituted sheet) that result in different rates of menthol migration to the filters of cigarettes made from a single tobacco type.

p. Different tobacco types smolder at different rates. This difference affects the distribution of menthol and probably all additives between MS and SS.

q. For most efficient menthol transfer, the optimum triacetin level on CA filters is around 5% to 6%.

r. Menthol is transferred to smoke more efficiently from a mentholated filter than from a mentholated blend.

s. Menthol is eluted more efficiently from a filter without triacetin, but, even with triacetin, menthol in the filter is about twice as likely to be delivered to MS as is menthol in the tobacco column.

t. For unfiltered cigarettes or cigarettes with filters lacking appreciable menthol affinity, significant amounts of menthol will migrate to the cigarette packaging materials resulting in reduced menthol available for transfer to MS.

u. At given plasticizer and filter ventilation levels, as filter draft increases menthol transfers decrease.

v. Menthol transfer at a given FTC 'tar' yield depends on the particular combination of filter draft and ventilation level.

w. As 'tar' increases, menthol transfers increase at all ventilation levels

x. At lower draft levels, menthol per unit 'tar' increases with ventilation but at higher draft levels there is no effect of ventilation.

y. Although adjustment of cigarette parameters can be used to affect menthol transfer, when the 'tar' yield and tobacco menthol load is arbitrarily fixed, the range of control is extremely limited.

REFERENCES

1. Best, F. W., Perfetti, T. A. and Sink, T. S. 1992. R. J. Reynolds Tobacco Company. Internal data.
2. Brozinski, M., Dolberg, U. and Lipp, G. 1972. Distribution of menthol in tobacco, filter, and smoke from menthol cigarettes. *Beiträge zur Tabakforschung International*. 6(3):124-130.
3. Curran, J. G. 1972. Delivery of menthol from cigarettes containing either a mentholated filter or mentholated tobacco. *Tobacco Science*. 26:40-42.
4. Curran, J. G. 1975. Effect of certain liquid filter additives on menthol delivery. *Tobacco Science*. 19:69-70.
5. Curran, J. G. The effect of filter surface area, filter weight, plasticizers, plasticizer concentration, and storage time on menthol migration from the tobacco to an acetate filter of a filter cigarette. Eastman Kodak Company, Publication No. FTR-21.
6. Curran, J. G. Effect of triacetin on menthol delivery of experimental cigarettes with Filtrona's SCS filter. Eastman Chemicals. Unpublished data.
7. Deutsch, L. J. 1990. Menthol behavior in the filter cigarette: 1. The dependence of menthol migration and delivery on the site of application. 44th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina.
8. Dube, L. G. 1982. R. J. Reynolds Tobacco Company. Internal data.
9. Eble, A. S. 1987. The effects of migration and elution on menthol delivery in cigarettes. *Proceedings of the International Conference on the Physical and Chemical Processes Occurring in a Burning Cigarette*. R. J. Reynolds Tobacco Company, Winston-Salem, North Carolina, pp 261-279.
10. FPB-11. 1992. Technical Bulletin. Filter Products Division, Hoechst Celanese Corporation.
11. Green, C. R., Conrad, F. W. and Dube, M. F. 1982. R. J. Reynolds Tobacco Company. Internal data.

12. Jenkins, R. W., Newman, R. H. and Chavis, M. K. 1970. Cigarette smoke formation studies II. Smoke distribution and mainstream pyrolytic composition of added ^{14}C-menthol (U). *Beiträge zur Tabakforschung International*. 5:299-301.

13. Lewis, L. S. and Norman, A. B. 1985. R. J. Reynolds Tobacco Company. Internal data.

14. Mangan, P. P. 1992. R. J. Reynolds Tobacco Company. Internal data.

15. Mathis, D. E. 1983. Migration and delivery of filter favors. *Beiträge zur Tabakforschung International*. 12(1):1-8.

16. Mitchell, B. C., Barbee, E. P. and Irby, Jr., R. M. 1963. Chromatographic determination of menthol in cigarettes and cigarette smoke. *Tobacco Science*. 7:64-66.

17. Newell, M. P., Latimer, P. H. and Haefele, L. R. 1968. The fate of menthol in cigarette smoke. 22nd Tobacco Chemists' Research Conference, Richmond, Virginia.

18. Norman, A. B., Perfetti. T. A., Poe, M. E. and Newsome, J. B. 1984. R. J. Reynolds Tobacco Company. Internal data.

19. Norman, A. B. and Townsend, D. E. 1982. R. J. Reynolds Tobacco Company. Internal data.

20. Park, J. Y., Yang, K. K. and Yu, K. K. 1979. A study of the effect of menthol added to the filter. *Journal of the Korean Society of Tobacco Science*. 1(2):149-151.

21. Perfetti, T. A. 1985. R. J. Reynolds Tobacco Company. Internal data.

22. Perfetti, T. A. and Gordin, H. H. 1985. Just noticeable difference studies of mentholated cigarette products. *Tobacco Science*. 29:57-66.

23. Perfetti, T. A. and Teot, K. M. 1986. R. J. Reynolds Tobacco Company. Internal data.

24. Renfro, L. W. 1990. Mechanisms of menthol delivery in filter cigarettes. 44th Tobacco Chemists' Research Conference, Winston-Salem, North Carolina.

25. Riehl, T. F., Shockley, L. L. and Reynolds, M. L. 1973. Menthol distribution and transfer. *Tobacco Science*. 17:10-11.

26. Schmeltz, I. and Schlotzhauer, W. S. 1968. Benzo[a]pyrene, phenols and other products from pyrolysis of the cigarette additive, (d,l)-menthol. Nature. 219:370-371.

27. Shofner, R. A and Ireland, M. S. 1982. Rapid analysis of menthol and nicotine in smoke and the effects of air dilution on delivery. *Tobacco Science*. 26:109-112.

28. Strickler, D. V. 1989. Effect of age on the menthol and triacetin delivery of mentholated cigarettes. CORESTA Technical Group, Interlaken, Switzerland.

29. Townsend, D. E. Personal communication.

30. Whitton, T. A. and McAdam, K. G. '1991. Factors influencing the transfer of menthol from cellulose acetate filters. 45th Tobacco Chemists' Research Conference, Asheville, North Carolina.

31. Wong, M. M., Durham, J. R. and Lawrence, B. M. 1988. R. J. Reynolds Tobacco Company. Internal data.

32. Woods, C. E. 1983. Cellulose acetate filter and fiber parameters affecting cigarette menthol delivery and menthol absorption by the filter tip. 37th Tobacco Chemists' Research Conference, Washington, D. C.

SYMPOSIUM SUMMARY

Thomas A. Perfetti

R. J. Reynolds Tobacco Company
Bowman Gray Technical Center
P. O. Box 1487
Winston-Salem, NC 27102

The history, science and technology surrounding the topics of menthol and mentholated cigarettes are exciting and challenging. Our speakers have allowed us to travel with them through history during this symposium. Many of you have walked the path of this journey and have contributed to our overall understanding of menthol and mentholated cigarettes. Many of the pioneers who first experimented with the development of mentholated cigarettes are no longer with us. Hopefully, we have represented them well. The record of this symposium will be a valuable resource for the future as well as a valuable contribution to an already rich historical record dealing with tobacco and smoke chemistry.

I am certain we all are thankful to our speakers for the excellent reviews which they have shared with us.

Let me thank the Program Editorial Committee of this TCRC for asking me to chair this symposium. I feel very honored to have worked with all of the speakers over the last few months on an area of science that I truly enjoy.

As I introduced the symposium with a provocative thought, let me leave the symposium considering the words of Eric Hoffer, the Longshoreman Philosopher:

> "In times of change, learners inherit the earth, while the learned find themselves beautifully prepared to deal with the world that no longer exists."

INFORMATION FOR ORDERING PREVIOUS SYMPOSIA

FREQUENCY: Annual. One volume number per year.

PUBLISHER: The Tobacco Chemists' Research Conference

ORDER FROM THE DISTRIBUTOR:

Tobacco Literature Service
2314 D. H. Hill Library, Box 8009
North Carolina State University
Raleigh, North Carolina 27695-8009 USA
Telephone: (919) 515-2836

Telephone orders not accepted, but inquires are welcome.

TERMS:

1. All orders MUST be prepaid.
2. Invoice sent upon request.
3. Payment accepted ONLY in U. S. currency or with a check drawn on an American bank. Foreign subscribers who pay through an American bank should instruct the bank to include the following information with payment:
    a. Publication being ordered.
    b. Number of copies wanted.
    c. Correct shipping address. Checks received without this information will be returned to the bank for instructions.
4. UNESCO coupons not accepted.

SUBSCRIPTIONS: Accepted.

BACK NUMBERS: Inquire for availability.

REFUNDS: Not allowed.

DISCOUNTS: Not available. No discount for multiple copies or to agents.

PRICES: U. S./Canada/Mexico: $27.00 per volume including postage and handling. All other locations: $41.00 per volume.

SHIPMENT: All shipments sent surface; postage is included in purchase price. Customers who require air shipment should request a price quotation.

CONTENTS: Each volume concerns a particular topic in tobacco chemistry.

PHOTOCOPY SERVICE: The Tobacco Literature Service does not provide copies of individual papers from the Conference Proceedings. Copies of papers presented at the Conferences but not reproduced in the Proceedings are not available from the Tobacco Literature Service, although the author's address may be available.