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Status Report on the Efforts by Hairspray Manufacturers to Comply with the 1998 VOC Standard of 55 Percent

For Discussion at Public Workshop
April 30, 1996

Stationary Source Division

California Environmental Protection Agency
Air Resources Board

DRAFT

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[1] Copies of the appendices are not available on this system, but may be obtained by contacting Mr. Edward Wong, Associate Air Pollution Specialist at (916) 327-1507

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I. INTRODUCTION

This report presents our assessment of manufacturers' progress in complying with the 55 percent volatile organic compound (VOC) hairspray standard established in the consumer products regulation.

II. CONCLUSIONS AND RECOMMENDATION (TO BE ADDED)

III. BACKGROUND

Hairsprays are aerosol or pump products designed for dispensing droplets of resin (film forming polymer) on and into the hair coiffure to enable users to keep their hair in position for a period of time. The key ingredients in hairspray formulations are resins, solvents, propellents (aerosols) and miscellaneous other ingredients such as neutralizers, fragrances, and plasticizers. Of these, the propellent and solvents are the main contributors to VOC emissions. Hairsprays are a significant source of VOC emissions in California and are the largest single source of consumer product emissions, with 46 tons/day VOC emissions estimated for 1990 in the Technical Support Document for the original consumer products rulemaking.

To realize emission reductions from this significant source, the Air Resources Board (ARB or Board) established a two tier standard for hairsprays when they adopted the consumer products regulation. Beginning in 1993, manufacturers of hairsprays were limited to 80 percent VOC content for both aerosol and pump hairsprays. This is followed by a reduction in the VOC standard to 55 percent effective January 1, 1998. When the Board adopted the consumer products regulation they recognized that the 55 percent VOC hairspray standard would present formulation challenges to manufacturers. Because of this, the Board directed the ARB staff to monitor and provide periodic reports on industry's progress in meeting the future effective VOC standard.

The emission reductions realized by the hairspray standards are significant. The 80 percent VOC standard results in approximately a 7.2 ton per day statewide reduction in VOCs; the 1998 55 percent VOC standard will result in an additional 14.2 tons per day reduction. Both of these standards are now federally enforceable as part of the State Implementation Plan (SIP) since the consumer products regulation was approved as a SIP revision early in 1995.

On October 19, 1995, a group of hairspray manufacturers and raw material suppliers from the Cosmetic, Toiletry and Fragrance Association (henceforth "CTFA Hairspray Group") met with the ARB staff to discuss the issues and problems they have encountered in meeting the 55 percent VOC standard. Overall, they believed that they could meet the 55 percent challenge but would need additional time beyond 1998. Specifically, they requested the standard be postponed until the year 2002 and that the ARB review industry's progress in the year 2000 and provide a report to the Board.

To address the Board's directive, and to respond to the request of the CTFA Hairspray Group, we prepared this draft report outlining our findings on manufacturers' progress in developing 55 percent VOC hairspray formulas. The remainder of this report includes a summary of the sources of data used to prepare the report, our findings, the conclusions that can be drawn from the findings, our recommendation (to be added) and a discussion on the SIP issues that potentially could result from modification to the standard.

IV. PROCESS FOR GATHERING DATA

In writing this draft report, information and data was compiled using various sources including trade journals, books, patents, the Consumer Products Registration Database, teleconferences and meetings with industry.

The Consumer Products Registration Database was valuable in supplying ARB staff with contacts for hairspray manufacturers. This database contains the names, locations, and telephone numbers for 78 hairspray manufacturers, which were used to contact manufacturers to inquire on the status and progress of their efforts to reach the upcoming 55 percent VOC limit for hairspray. These manufacturers are listed in Table 1.

Through phone conversations or teleconferences with various manufacturers, we were able to gather information on individual manufacturer's efforts in developing 55 percent VOC hairsprays. We contacted 30 hairspray manufacturers and ten raw material suppliers during our evaluation.

In addition, the nine CTFA Hairspray Group member companies which met with ARB staff on October 19, 1995 also provided valuable information on their experiences in working toward developing a 55 percent VOC hairspray. The group was comprised of five hairspray manufacturers, and four raw material/package suppliers, along with representatives from the Cosmetic, Toiletry and Fragrance Association. Members present at the October 19, 1995 meeting included The Gillette Company, Chesebrough-Pond's USA Company, Helene Curtis, Procter and Gamble, Cosmair, BASF Corporation, National Starch and Chemical Company, International Speciality Products, and Calmar Incorporated.

Technical reports and articles found in industry trade journals and other literature were reviewed. A list of the trade journals and printed literature used by staff in developing this report is presented in Table 2.

Finally, a search of the patent literature provided useful data on recent patents for 55 percent VOC hairspray formulations. Only those patents that were assigned in 1992 or beyond were considered. Seventeen patents were found that addressed 55 percent or lower VOC hairspray formulations. These patents are identified in Table 3.

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TABLE 1

HAIRSPRAY MANUFACTURERS REPORTING INFORMATION IN THE CONSUMER PRODUCTS REGISTRATION DATABASE

Company Names

Aerosol Services Company, Inc/Nexxus Pro
Amway Corporation
Calvin Klein Cosmetics Company
Chuckles, Incorporated
Clairol Incorporated
Conair Corporation
Cosmosol, LTD
The Dial Corporation
E T Brown Drug Company, Incorporated
Focus 21 International
Gelle' International, Ltd. (Key Distrib)
The Gillette Company
Goldwell Cosmetics (USA), Incorporated
H2O Plus Inc/Hydrotech Labs
Head First, Incorporated
IQ Products Company/Formally-CSA Limit
Joed Cosmetics Research
John Paul Mitchell Systems
KMS Research, Incorporated
Key Distributors, Incorporated
L & F Products
La Costa Products International
Longs Drug Stores
Majestic Drug Company, Incorporated
Matrix Essentials, Incorporated
Modern Research
National Aerosol Products Company
NuSkin International
Penn Champ, Incorporated
Premiere Products, Incorporate
Professional Choice Lab
Redkin Laboratories
Revlon, Incorporated
Salon Technology, Incorporated
Stores
Schwarzkopf, Incorporated
Sebastian International, Incorporated
St. Ives Laboratories
Thrifty Corporation
The Wella Corporation

Alberto-Culver, Inc
Aveda Corporation
Chesebrough-Ponds USA Company
Claire MFG Co./Sprayaway Products
Compare Value Products
Cosmair, Incorporated
DEP Corporation
Dow Brands
Estee Lauder Companies
Gar Labs, Incorporated
Georgette Klinger, Incorporated
Golden Sun, Incorporated
Graham Webb International
Hair Muscle, Incorporated
Helene Curtis, Incorporated
Image Laboratories, Incorporated
John Frieda, Incorporated
Joico Laboratories, Incorporated
Kenra Laboratories, Inc, / Elasta Products
Key West Aloe, Incorporated
L'anza Research International, Incorporated
Lander Company, Incorporated
M J Eckhard, Incorporated
Mary Kay Cosmetics, Incorporated
Merle Norman Cosmetics
N M Barr and Company, Incorporated
Nexxus Products Company
Pantresse, Incorporated
Peter Thomas, Incorporated
Procter & Gamble Company
Promotional Products Development, Inc.
Regis Corporation
Revlon-Realistic
Savon Division of American Drug

Scruples Professional Salon Products
Shaklee U.S., Incorporated
Target Stores
Vital Care of North America, Ltd. (Key D)
Zotos International, Incorporated

TABLE 2

TRADE JOURNALS AND BOOKS

Drugs and Cosmetics Industry
Household and Personal Products Industry
Cosmetics & Toiletries
Spray Technology & Marketing
Chemical and Physical Behavior of Human Hair, Clarence R. Robbins, 1994 by Springer-Verlag New York, Incorporated
DuPont Dymel Aerosol Propellants, Dymel®/Aerosol Technical Course

TABLE 3
HAIRSPRAY FORMULATION PATENTS MEETING THE 55 PERCENT VOC STANDARD

Ref #	Patent #	Date	Assignee	Title
1)	5,413,775	May 9, 1995	Amerchol Corporation	Hairsprays and Acrylic Polymer Compositions For Use Therein (P, A)*
2)	5,304,368	April 19, 1994	American Telecast Corporation	Non-Foaming, Non-Viscous, Alcohol-Free, Water-Based Pressurized Hair Spray Product (A)
3)	5,441,728	August 15, 1995	Chesebrough-Pond's, USA Company	Hairspray Compositions (P, A)
4)	5,266,308	November 30, 1993	Chesebrough-Pond's, USA Company	Hair Treatment Composition (P, A)
5)	5,314,684	May 24, 1994	Clairol, Incorporated	Water-Based Fixative Composition (P)
6)	5,320,836	June 14, 1994	Eastman Kodak Company	Hair Spray Formulations Containing A Polyethylene Glycol Ester of Caprylic and Capric Acids (P, A)
7)	5,266,303	November 30, 1993	Eastman Kodak Company	Aerosol Hair Spray Formulations (A)
8)	5,286,477	February 15, 1994	Helene Curtis, Incorporated	Aerosol Hair Styling Aid (A)
9)	5,164,177	November 17, 1992	Helene Curtis, Incorporated	Aqueous Hair Styling Aid (P, A)
10)	5,326,555	July 5, 1994	ISP Investments, Incorporated	Clear Hair Spray Composition Capable of Forming Low Tack Films Which Dry Rapidly (P, A)

Note: A = Aerosol, P = Pump

TABLE 3 (cont.)
HAIRSPRAY FORMULATION PATENTS MEETING THE 55 PERCENT VOC STANDARD

Ref #	Patent #	Date	Assignee	Title
11)	5,275,811	January 4, 1994	ISP Investments, Incorporated	Hair Spray Resin Composition (P, A)
12)	5,223,247	June 29, 1993	ISP Investments, Incorporated	Hair Spray Composition Containing Water Soluble Alkylated PVP Copolymers as Hair Fixative Therein (P, A)
13)	5,221,531	June 22, 1993	ISP Investments, Incorporated	Polymer Hair Fixatives, Aqueous-Based Solution Process for Making Same and Water-Based Hair Spray Formulations Therewith Which Meet VOC Standards (A)
14)	5,182,098	January 26, 1993	ISP Investments Incorporated	Terpolymer Hair Fixatives, Aqueous Solution Process for Making Same and Water-Based Hair Spray Formulations Which Meet VOC Standards (A)
15)	5,160,729	November 3, 1992	ISP Investments, Incorporated	High Water Content Hair Spray Composition (P, A)
16)	5,158,762	October 27, 1992	ISP Investments, Incorporated	Water-Based Hair Spray Compositions Containing Multiple Polymers (P)
17)	5,126,124	June 30, 1992	ISP Investments, Incorporated	Hair Spray Resin Composition (P, A)

Note: A = Aerosol, P = Pump

V. FINDINGS

This section presents a summary of ARB staff findings regarding manufacturers' efforts in developing 55 percent VOC hairsprays. The first section discusses the challenges identified by the CTFA Hairspray Group in meeting the 55 percent VOC hairspray standard by January 1, 1998. The second through fifth sections describes information on possible 55 percent VOC formulations gleaned from patent searches, technical literature reviews, manufacturer contacts, and raw material supplier contacts, respectively. The final section describes several possible 55 percent VOC aerosol formulations and their estimated materials cost.

A. Cosmetic, Toiletry and Fragrance Association Hairspray Group Meeting Summary - October 19, 1995

At the request of CTFA, staff of the Stationary Source Division (SSD) met with representatives from CTFA and 9 member companies on October 19, 1995. Attendees included CTFA staff and representatives from the following member companies: The Gillette Company, Chesebrough-Pond's USA Company, Helene Curtis, Incorporated, The Procter and Gamble Company, Cosmair, BASF Corporation, National Starch and Chemical Company, International Speciality Products, and Calmar, Incorporated. CTFA requested this meeting to provide an opportunity for discussion on the issues and problems the attending companies were having in meeting the 55 percent VOC standard for hairsprays. Six presentations were provided to SSD staff entitled: "Presentation to CARB 55% VOC Issues," "55% VOC Non Aerosol Hair Spray Presentation to the California Air Resources Board," "55% VOC Aerosol Hairsprays Presented To CARB Oct, 19, 1995," "Fundamental Challenges Of 55% VOC Hairsprays," "Low VOC Hair Spray Presentation to California Air Resources Board," and "Hairsprays." A brief summary of the presentations and the ensuing discussion is presented below (copies of these presentations are included in Appendix A).

According to the manufacturers present at the meeting, VOC reductions in aerosol and pump hairsprays will be achieved by decreasing the alcohol and or propellants in aerosols and the alcohol in pumps. In most cases, this will result in an increase in water content of the formula. Increasing the water content of a hairspray formula is a viable solution, but causes concern because water creates several problems. The problems created with the addition of water to existing hairspray formulas were discussed and included: resin solubility, increased viscosity, drying time, initial curl droop, tackiness, loss of holding power, changed spray characteristics, humidity and curl resistance. In addition, the manufacturers expressed concern that increasing the water content of hair spray can also cause can corrosion and solvent/propellant incompatibility. The more problematic performance characteristics identified by the group included initial curl droop, spray characteristics, and resin solubility.

Initial curl droop, which is the relaxation of a curl occurring between the time a hairspray is initially applied and the time when the hairspray is dry enough to hold the curl in place is one of the main concerns for these hairspray manufacturers. Initial curl droop is a hairspray efficacy test developed for testing 55 percent VOC hairspray products by measuring the amount of hair droop after spraying a curl formed from a straight, unprocessed hair strand. The test performed in ambient conditions, provides a method to measure the differences in hairsprays. They explained in detail that the cause of curl droop is the breaking of hydrogen bonds by the water in low VOC formulas. Hydrogen bonds are created during the styling process and are what hold a style in place until a hairspray can create a permanent hold. They

also stated that there is no standardized method to measure initial curl droop and each company uses its own method or assessment of what a hairspray's performance should be to meet consumer expectations. As a general rule, most of these manufacturers are striving to develop 55 percent VOC products that have performance characteristics equal to or better than the 80 percent hairspray formulas.

Increasing the water content of a hairspray formulation can result in increased solution viscosity and surface tension. This in turn can affect the spray characteristics of the hairspray. In particular, increased viscosity and surface tension result in larger droplet sizes and affect the distribution of the hairspray resin on the hair shaft. Another problem that results from the increased viscosity is the need for more mechanical energy to atomize the hairspray formula than current technology is capable of providing. The manufacturers present believe that new pump/valve systems will need to be developed to overcome this problem.

Resin solubility was another concern for these manufacturers. According to the manufacturers present, available resins are not compatible with large amounts of water. It was the consensus of this group that new resins are needed that can tolerate high water content. Ideally, these resins would have small hydrodynamic volumes which will allow for molecular unfolding and entanglement during drying to provide film formation while preventing osmotic intrusion of water into the hair fiber. This would allow for good immediate spread along the hair and between the hair fibers while maintaining desired droplet size distribution.

Overall, the manufacturers and raw material suppliers present at the meeting believe that low VOC hairsprays are feasible but will require new resins and dispensing systems before they can be successfully formulated. At this time, they indicate they do not know how to address all the problems involved in incorporating large amounts of water into hair spray formulations and believe additional technology development is necessary. They do not see the problems resolvable in the near future and proposed that a more realistic approach would be for the 55 percent VOC standard to be extended to 2002, provided the ARB would commit to an evaluation of progress in the year 2000.

The ARB staff recognize that these manufacturers are in the business of producing and marketing products which satisfy consumer demands. The successful marketing of 55 percent VOC products broadly meeting consumer demands relies on an in-depth knowledge of consumers and the marketplace, for which hairspray manufacturers clearly are the experts. While the information presented in this report demonstrates substantial progress toward formulating viable 55 percent VOC products, the data provided by these manufacturers indicate that many companies need more time to develop optimal products which can satisfy their particular market niches. In recognition of the manufacturers' need to formulate widely-acceptable products, the ARB staff have concluded that it is appropriate to explore options that would provide some additional time for reformulation provided: (1) the SIP is kept intact, and (2) those companies that have been successful in developing low VOC products would not be disadvantaged.

B. Patent Search Summary

Summary of Findings:

There were 17 patent references found that were assigned in 1992 or beyond. These patents are listed in Table 3. Of the 17 patents, five apply to aerosol compositions, two apply to pump compositions, and ten apply to both aerosol and pump compositions. The Amerchol Corporation, American Telecast Corporation, and Clairol, Incorporated each hold one patent, Chesebrough Pond's USA Company, Eastman Kodak Company, and Helene Curtis, Incorporated each hold two patents, and ISP Investments, Incorporated holds the remaining eight patents. The Amerchol Corporation, American Telecast Corporation, Eastman Kodak Company, and ISP Investments, Incorporated are raw material suppliers whereas Chesebrough Pond's USA Company, Clairol, Incorporated, and Helene Curtis, Incorporated are hairspray manufacturers.

The patents contain information for developing a range of hairspray compositions, including 55 percent VOC sample compositions that are claimed to be successful in meeting one or more of the following performance characteristics: curl retention, dry time, feel, flaking, brittleness, humidity resistance, luster, gloss, particle size, rinsability, spray pattern, spray rate, tack, and viscosity. The low-VOC compositions claimed in the patents basically consist of a fixative polymer, solvent (primarily water and/or some alcohol), propellant in aerosols (primarily dimethyl ether), and adjuvants. A general description of each patent is provided below.

Findings:

Aerosol Patents

Five aerosol patents were found and are listed as Reference # 2, 7, 8, 13, and 14 in Table3. The name of the assignees and number of aerosol patents they each hold are as follows: American Telecast Corporation (1), Eastman Kodak Company (1), Helene Curtis, Incorporated (1), and ISP Investments, Incorporated (2).

The American Telecast Corporation (ATC) was assigned a patent (Table 3, Reference #2), for a non-foaming, non-viscous, alcohol-free, waterbased hairspray in an aerosol container which is delivered from an actuated-valve of predetermined dimensions, and is suitably titled "Non-Foaming, Non-Viscous, Alcohol-Free, Water-Based Pressurized Hair Spray Product." The optimum composition range, in weight percent, consists of shellac (2.5-3.5%), synthetic resin (5.5-6.5%), neutralizer for shellac and synthetic resin (1.5-2.25%), dimethyl ether (DME) (38-40%), and water (remainder of fill weight). The ATC patent cites 26 other patents which describe fixative polymers which may be used as co-resins in their compositions, with a particularly useful fixative resin being the polymer Amphomer LV-71 produced by National Starch and Chemical Corporation. A plasticizer (1-5%) may also be included, and if desired, about 0.1-0.5 percent of the total fill of one or more of a perfume oil, fragrance, antimicrobial agent, biocidal agent, buffer, antioxidant, coloring agent, anticorrosive agent, aloe plant extract, or mixtures thereof, giving a composition pH of about

9.

In a detailed description of the invention, the ATC patent describes the preparation of a hairspray composition consisting of 60 percent concentrate (having up to 82 parts water, by weight) and 40 percent DME. This composition was applied on ten different hair samples and it was found that the percent curl retention varied from 75 to 85 percent. The patent also claims the hairspray composition provides satisfactory combability, feel, sheen, luster, and flaking after two combings; an advantageous spray delivery rate (0.2-0.25 grams/second) and particle size (50 $\pm$ 12 microns); uniform can evacuation without clogging; and a relatively dry spray to decrease drying time. According to the patent, the advantageous features of the invention were recognized during several salon testings between it and seven commercial aerosol and pump hairsprays, which included both waterbased and alcohol-containing compositions. In addition, according to the patent, the waterbased composition of the invention was considered the hairspray product of choice by the salon operators who participated in the tests.

Two of the aerosol patents employ the use of terpolymers. One patent (Table 3, Reference #8) assigned to Helene Curtis, Incorporated (HC) is for an aqueous hairspray styling aid composition and is titled "Aerosol Hair Styling Aid." It consists of a terpolymer (consisting of vinyl pyrrolidone, ethyl methacrylate and methacrylic acid monomers), which is at least partially neutralized for water solubility, in amounts from 2-8 percent, by weight, of the total fill, water (30-80%), DME (25-35%), and ethanol (5-25%), being optimally included for fast drying. The terpolymer was originally designed for use as a fixative polymer for pump sprays because apparently it was found to be incompatible with hydrocarbon propellants or required too much alcohol as a solvent to satisfy VOC regulations. However, according to the patent, it has been found that with the use of DME as the propellant, excellent and homogeneous delivery of the terpolymer could be achieved. Other polymers may be added to aid solubility and dispersability in water for the terpolymer.

Additionally, the HC patent lists numerous compounds which may be suitable components in the hairspray composition as water-insoluble conditioning agents, suspending agents, thickening agents, or emulsion stabilizers. The hairspray compositions can also contain a variety of other nonessential optional components suitable for rendering the compositions more acceptable such as other emulsifiers, preservatives, thickener and viscosity modifiers, pH adjusting agents, coloring agents, hair oxidizing agents, hair reducing agents, perfume oils, chelating agents, or polymer plasticizers.

In the HC patent four samples are provided which are claimed to be suitable compositions with the invention. The water content in these compositions range from 35-57 percent, by weight. An example of one sample composition with little or no alcohol is as follows: terpolymer of vinylpyrrolidone/ethyl methacrylate/methacrylic acid fixative resin (12%), neutralizing agent such as 2-methyl-2-amino-1-propanol (1%), ethyl alcohol (5%), DME (25%), water (56.73%), dimethicone (0.15%), and fragrance (0.12%). Although the patent claims that one aspect of the invention provides hair setting compositions for retaining a particular shape or configuration of the hair, no specific information or test results is provided to substantiate the claims.

The other patent (Table 3, Reference #14) which employs the use of a terpolymer hair fixative is assigned to ISP Investments, Incorporated (ISP) and is titled "Terpolymer Hair Fixatives, Aqueous Solution Process for Making Same and Water-Based Hair Spray Formulations Which Meet VOC Standards." This patent provides for an aqueous solution process for making the terpolymer and for developing waterbased hairspray formulations which meet VOC standards. The terpolymer consists of vinyl caprolactam (VCL), vinyl pyrrolidone (VP), and methacrylamidopropyl trimethylammonium chloride (MAPTAC). The patent explains that while the mechanism of synergistic action of the three components of the terpolymer is not completely understood at present, it is believed that the presence of the VCL monomer provides a hydrophobic component which enhances the humidity resistance and hold of the hairspray composition while retaining the desired water solubility of the terpolymer and allowing its preparation by an aqueous solution process.

There are four low-VOC compositions that are provided in the patent, one alcohol-containing and three nonalcohol-containing hairspray formulations. The alcohol-containing formulation is comprised of a terpolymer solution (10%), water (45%), ethanol-anhydrous (10%), and DME (35%). The patent claims that this formulation was tested in what it refers to as the conventional manner for hold (curl retention at 90 percent relative humidity and 80 degrees Fahrenheit) and showed 85 average percent curl retention after 90 minutes of treatment. Each of the three nonalcohol-containing formulations contain the same amount of polymer (10%), but a different weight ratio of VCL/VP/MAPTAC, and the same amount of water (55%) and DME (35%). The patent claims that these compositions showed a 70 percent curl retention after 90 minutes of treatment. Suitable composition ranges may be as follows: terpolymer (3-6%), water (15-50%), DME (30-35%), and ethanol (0-10%). While no specific testing information is provided, the patent states that the waterbased hairspray compositions of the invention exhibit excellent performance characteristics.

ISP Investments, Incorporated holds another patent (Table 3, Reference 13) for aerosols and it is titled "Polymer Hair Fixatives, Aqueous-Based Solution Process for Making Same and Water-Based Hair Spray Formulations Therewith Which Meet VOC Standards." This patent provides for a polymer hair fixative comprising of VCL, VP, dimethylaminoethyl methacrylate (DMAEMA) and acrylic acid (AA), a process for preparing such polymers in an aqueous or aqueous-alcoholic solvent where the viscosity of the polymer product can be controlled in a predetermined manner, and where waterbased hairspray compositions can be produced to meet VOC standards. According to the patent, the mechanism of synergistic action of the four components of the polymer is not completely understood at present, however, it is believed that the VCL monomer provides a hydrophobic component which enhances the humidity resistance and hold of the hairspray composition and the AA component further enhances the water solubility of the product thus providing better removability after use.

There are four low-VOC compositions that are provided in the patent, one alcohol-containing and three nonalcohol-containing hairspray formulations. The alcohol-containing formulation is comprised of a polymer solution (10%), water (45%), ethanol-anhydrous (10%), and DME (35%). Similar to the ISP patent described above for terpolymers, this formulation was tested in the conventional manner for hold. The test results showed 85 average percent curl retention after 90 minutes of treatment. Each of the three nonalcohol-

containing formulations contain the same amount of polymer (10%), but a different weight ratio of VCL/VP/DMAEMA/AA, and the same amount of water (55%) and DME (35%). It is claimed that these compositions showed a 70 percent curl retention after 90 minutes of treatment. According to the patent, the preferred composition range may be as follows: VCL/VP/DMAEMA/AA polymer (3-6%), water (15-50%), DME (30-35%), and ethanol (0-10%). While no specific testing information is provided, the patent states that the waterbased hairspray compositions of the invention exhibit excellent performance characteristics.

The final aerosol hairspray patent (Table 3, Reference #7) is assigned to the Eastman Kodak Company (EKC) and is titled "Aerosol Hair Spray Formulations." This patent relates to hairspray compositions based on (1) a sulfonate containing water dissipatable linear polyester (sulfo-polyester resin) having a glass transition temperature (Tg) between 36 degrees and 40 degrees Centigrade (C), (2) a water soluble, polyvinyl lactampolymer, (3) water, and (4) no VOCs other than the propellant. The composition range may be as follows: sulfo-polyester resin (1-10%), polyvinyl lactam polymer (1-7%), water, or water/alcohol mixture (46-94%), and DME, or hydrocarbon propellant, or mixtures thereof (3-40%). Other conventional additives may be preservatives, fragrances, antifoaming agents, hair conditioners, and plasticizers.

Four hairspray compositions are provided in the EKC patent, two having a sulfo-polyester resin with a Tg of 38 degrees C, and 1 of each composition having a sulfo-polyester resin with a Tg of 30 and 55 degrees C. The composition with a sulfo-polyester resin with a Tg of 30 degrees C has an identical formulation to that of one of the compositions with a sulfo-polyester resin with a Tg of 38 degrees C. In subjective testing, the identical hairspray compositions having a sulfo-polyester resin with a Tg of 30 and 38 degrees C, were applied on hair trusses and compared. According to the patent, the formulation containing a sulfo-polyester resin with a Tg of 38 degrees C was significantly superior in terms of being less tacky or sticky. In addition, the patent claims that this formulation had good rinsability, washability, and humidity. Other desirable features stated in the object of the patent are fast drying time, acceptable body, consistency and firm texture necessary to hold hair in the desired arrangement for a certain length of time, excellent storage stability, and no clogging or foaming from the aerosol container. The hairspray composition having a sulfo-polyester resin with a Tg of 55 degrees could not be tried because the sulfo-polyester resin precipitated in the presence of DME or ethane.

Based on the preparation described for the successful hairspray formulation having a sulfo-polyester resin with a Tg of 38 degrees C, ARB staff calculated its composition to be 10.3 percent resin, 41.7 percent water, 28 percent ethanol, and 20 percent propellant, or approximately 48 percent VOC by weight. The untested hairspray composition having a sulfo-polyester resin with a Tg of 38 degrees C is calculated to have 9 percent resin, 61 percent water, and 30 percent DME (30% VOC).

Pump Patents

Two pump patents were found and are listed as Reference #5 and 16 in Table 3. The name of the assignees are Clairol, Incorporated and ISP Investments, Incorporated.

The first pump patent (Table 3, Reference #5) assigned to Clairol, Incorporated (CI) is titled "Water-Based Fixative Composition." It is a hair fixative composition that contains a water-dispersible amorphous thermoplastic hair fixative polyester. The fixative polyester is in colloidal suspension in the composition. The preferred polymeric hair fixatives for the CI compositions are the Eastman Chemicals AQ Polymers, especially the AQ-55 Polymers. Such compounds form hard, clear films without the need for solvents, and more specifically, the Eastman Chemicals AQ Polymers are relatively high molecular weight, amorphous polyesters that disperse directly in water without the assistance of organic co-solvents, surfactants, or amines.

The composition further contains a copolymer containing dimethyl polysiloxane and organo-modified methylsiloxane moieties in such amount to sufficiently cause the composition to spread out on a hair shaft when the composition is applied to same. According to the patent, this copolymer is the key to providing an acceptable dispensing pattern and acceptable hairspray characteristics, and is referred to by the CTFA name, dimethicone copolyol. Also, according to the CI patent, the dimethicone copolyol produces an improvement in the reduction of wetness perception partly by reducing the surface tension of the composition allowing for the dispensing of smaller, more uniform, droplets. In addition, due to the surfactant properties of the dimethicone copolyol, a more uniform coating of resin on the hair shaft is quickly obtained and is evidenced by a reduction of clumping and matting of the hair. The dimethicone copolyol is available from Union Carbide, under the tradenames Silwet L-7600, L-7604, and L-7614, and from Dow Corning under the tradenames Silicone 190 Surfactant and Silicone 193 Surfactant.

The CI patent provides nine sample compositions, all of which contain water in an amount from 70-92 percent, by weight. These nine sample compositions also contain an Eastman Chemicals AQ Polymer in an amount from 4-8 percent. Six of the sample compositions were packaged in standard 6 fluid ounce plastic pump containers fitted with a commercially available pump sprayer. The six sample compositions were used and compared against a commercially available hair fixative pump spray (Clairol's Final Net) having a VOC of 88 percent, by weight. According to the patent, the salon test showed that under normal application rates, three of the sample compositions tested were perceived to dry as rapidly as the commercial product. The surface tension of these three compositions were very close to the Final Net hairspray (27.2, 28.6 and 26.9 dynes/centimeter versus 25 dynes/centimeter). The surface tension of the remaining three sample compositions tested were higher (31, 39 and 50.5 dynes/centimeter). The patent also claims that the six sample compositions tested performed as well as the comparative commercial product with regard to hair fixation. Accordingly, the most preferred composition ranges are as follows: water-dispersible amorphous thermoplastic polyester (5-7%), dimethicone copolyol (0.3-1.0%), alcohol, when present (1-25%), and water (remainder of fill). Other ingredients may be added as appropriate such as co-surfactants, co-solvents, co-fixatives, vitamins, and sunscreens.

The second pump patent (Table 3, Reference #16) is assigned to ISP Investments, Incorporated (ISP) and is titled "Water-Based Hair Spray Compositions Containing Multiple Polymers." According to this patent, the composition includes a predetermined blend of at least two hairspray resins, one being a water soluble resin and the other resin being a water dispersible polyester or polyesteramide. The patent suggests many kinds of monomers and terpolymers to prepare the water soluble resin. One preferred terpolymer is Gaffix VC-713 from GAF Chemicals Corporation. The ISP patent provides cites of U.S. patents which describe water-dispersible polyesters and polyesteramides which are available from Eastman Chemicals as the AQ-38 and AQ-55 Polymers.

The following hairspray composition was provided and tested as a pump spray: water (93.06%), Gaffix VC-713, 37 percent in ethanol (1.00%), Polymer AQ-55D (5.00%), PVP/VA W 735 Crovol A-70 (0.10%), panthenol (0.10%), Suttocide A (0.60%), Surfadone LP-300 (0.07%), fragrance (0.07%), and citric acid (as much as suffices). According to the patent, this formulation is a one-phase system and it was observed that the spray patterns developed were fine, broad and dry, with a soft hold, excellent shine, and low drying times. No further information was provided in the patent to substantiate the above claims. The composition ranges of the preferred embodiment is as follows: polymer blend of water soluble polymer and water dispersible polyester or polyesteramide (2-28%), water (40-98%), alcohol (0-30%), and neutralizing base (0-5%).

Aerosol/Pump Patents

The ten aerosol/pump patents are listed as Reference # 1, 3, 4, 6, 9, 10, 11, 12, 15, and 17 in Table 3. The name of the assignees and number of aerosol/pump patents they each hold are as follows: Amerchol Corporation (1), Chesebrough Pond's USA Company (2), Eastman Kodak Company (1), Helene Curtis, Incorporated (1), and ISP Investments, Incorporated (5).

The ten aerosol/pump patents provide a multitude of hairspray compositions that are applicable to both aerosols and pumps. While the various weight ranges may be as low as 10 percent for water and as high as 95 percent for alcohol, the compositions are primarily waterbased. The higher alcohol content reflects a few patents that provide for 80 percent as well as 55 percent VOC compositions. DME is the primary propellant suggested because of its ability to mix with relatively high amounts of water. However, other propellants may also be used such as hydrocarbon and compressed gas propellants. Similar to the compositions described for the aerosol patents and pump patents above, the compositions in the aerosol/pump patents are linked to the type of resins used. The ten aerosol/pump patents are described below.

The aerosol/pump patent (Table 3, Reference 1) assigned to the Amerchol Corporation (AC) is titled "Hairsprays and Acrylic Polymer Compositions for Use Therein." The resin system used here is an aqueous anionic, acrylic polymer composition comprised of a copolymer of an alkyl acrylate, an alkyl methacrylate and one or more acrylate acids or salts. The polymer composition is compatible in all-aqueous hairspray compositions as well as those that contain up to about 80 percent VOC or above. According to the patent, it has been found that by controlling the particle size of the copolymer and introducing certain types of surfactants in the final polymer composition, enhanced freeze-thaw stability of the polymer

composition can be obtained. It is stated that surfactants which are nonionic can provide enhanced freeze-thaw stability over surfactants which are ionic. The preferred weight percentages in the hairspray composition are as follows: polymer composition (3-15%), surfactant (0.1-0.3%), water (2-20%, 20-50%, 50-80%, and 80-99% depending on the concentration of the VOC), alcohol (0-50%), and in the case of aerosols, DME (35-45%). Additional ingredients in very minor amounts may be used such as emollients, lubricants, penetrants, proteins, dyes, tints, colorants, perfumes, and others.

If the hairspray composition is intended to be delivered by a pump system, the preferred VOCs, if present, are ethanol, isopropanol, or mixtures thereof, in amounts of 80 percent or less, less than 55 percent, less than 25 percent, and less than 1 percent. The AC patent states that the polymer composition has been found to provide excellent spray patterns, atomization characteristics, essentially no clogging, and full compatibility throughout the alcohol concentration range described above. if the hairspray composition is intended to be delivered by an aerosol system, the preferred propellant is DME at about 35-45 percent concentration. It has been found that within this range, enhanced spray patterns and drying times can be obtained as compared to other concentrations of 35 percent or less. Other propellants such as nitrogen and carbon dioxide can be used, with the balance of the carrier being water, a VOC such as ethanol, or mixtures thereof.

In the AC patent, 17 waterbased hairspray sample compositions were prepared and applied on hair tresses. A subjective evaluation of the hair tresses was made by a panel for combability, shine, flaking, natural feel, and curl retention. According to the patent, five of the hairspray compositions provided excellent performance for curl retention, which is considered to be one of the most important characteristics judged by the panelists. Within this group of five hairspray compositions, two also provided excellent shine and flaking resistance, one also provided excellent flaking resistance and natural feel, and one also provided excellent flaking resistance.

To test ethanol-containing compositions, three sample formulations were prepared using a polymer composition base from one of the above five compositions which tested excellent for curl retention. Using the polymer composition base, three hairspray compositions were prepared with ethanol concentrations of 0, 20, and 50 percent. The three ethanol compositions were compared against a commercially available hairspray, Final Net hairspray (regular hold). According to the patent, these compositions performed as good or better than the Final Net hairspray for curl retention, shine, and flaking resistance. Using the same polymer composition base as above, four hairspray compositions with 0, 20, 50, and 80 percent ethanol concentrations were applied on hair tresses and evaluated. According to the patent, all samples were found to have acceptable characteristics for spray pattern, drying time, tackiness, and flaking resistance.

Aerosol hairspray compositions were also prepared and tested. Three aerosol hairspray compositions were prepared using one polymer composition and three concentration levels of 1,1-difluoroethane (HFC-152a or Dymel A). The concentrations of HFC-152a were at 30, 40, and 45 percent. The aerosol formulations were tested and evaluated for spray pattern, drying time, and tackiness. It was found that the aerosol compositions with 40 and 45 percent HFC-152a provided an enhanced spray pattern, shorter

drying time, and less tackiness than the aerosol compositions with 30 percent HFC-152a.

The Chesebrough Pond's USA Company (CP) holds two aerosol/pump patents. The first CP patent (Table 3, Reference #3) is titled "Hairspray Compositions." This patent relates to an aqueous hair treatment composition that includes a water-soluble polymer having a solution viscosity at 10 percent water of less than about 20,000 centipoise at 25 degrees C, and a latex of water-insoluble polymeric particles dispersed in water and having a glass transition temperature (Tg) between -23 and +27 degrees C. The water-soluble polymers may be selected from nonionic, anionic, cationic, or amphoteric hair fixative polymers and be in the weight range of 1.5-10 percent. The water-insoluble polymeric particles may also range from 1.5-10 percent of the hairspray composition. Other ingredients include water (40-90%) and DME, hydrocarbon propellant (5-50%), or mixtures thereof, for aerosols.

The CP patent contains many examples of hairspray compositions which were tested for such characteristics as hair holding, rinsability, and gloss. In one set of tests, three hairspray formulations containing latex resin based on methylacrylate/butylacrylate latex were developed in waterbased aerosol and pump compositions. The physical properties and performance of these formulations were evaluated. The three aerosol hairspray compositions contained approximately 45 percent water and were compared against a 95 percent VOC alcohol-containing aerosol (aerosol control). According to the patent, two of the three sample compositions performed as good as the aerosol control for hair holding, rinsability, and gloss. The third sample composition was as good as the aerosol control for hair holding and rinsability, but had poor performance for gloss. The three pump sample compositions contained approximately 73 percent water and were tested against a 77 percent VOC alcohol-containing pump (pump control). Two of the three pump samples performed almost as well or slightly better than the pump control. The third pump sample performed as well or much better than the pump control for hair holding and gloss, but performed poorly with respect to rinsability.

In the CP patent, many other aerosol and pump hairspray compositions containing various latex resins were tested for hair holding, rinsability, and gloss. The results of the evaluations for these compositions indicated a balance of both good performing and poor performing formulations. In general, the testing of the hairspray compositions in the patent indicated that polymer latexes alone or the polymer blends containing polymer latex with a Tg either higher or lower than -23 and +27 degrees C were not suitable for hairspray applications.

The second patent (Table 3, Reference #4) held by CP is titled "Hair Treatment Composition." This patent is for a hair treatment composition that includes a water-insoluble, dispersible polymeric resin having a viscosity of less than 2 centipoise at 25 degrees C when dispersed at 10 percent in water, a water-soluble polymeric resin having a viscosity greater than 6 centipoise at 25 degrees C when 10 percent is placed in water, and a water-soluble polymer of molecular weight greater than about 500,000. According to the patent, each of the three components interacts with the other to provide an overall superior spray. The patent also states that the water-insoluble resin provides excellent hold, but is of low viscosity, the water-soluble resin has some hold, increases viscosity, and importantly aids in removing the water-insoluble resin from the hair upon shampooing, and the water-soluble polymer of molecular weight greater than 500,000 "optimizes the spray particles of the resin

combination".

The optimal concentration range of the water-insoluble resin in the hairspray composition is 2-6 percent and the preferred compound is the Eastman AQ-38S which is identified as a diglycol/cyclohexanedimethanol/isophthalates/sulfoisophthalates polyester. An effective water-insoluble resin suggested by the patent is the Luviskol VA 73W sold by the BASF Corporation. The optimal concentration range for this compound is 1.6-3.2 percent. The preferred concentration range for the third component, the water-soluble polymer of high molecular weight, is 0.05-0.2 percent (exclusive of the propellant). Water should be included in the range of 40-95 percent. Additional ingredients may include: neutralizing agents (0.001-10%), surfactant (0.3%), C10-C20 fatty alcohol esters (0.02-0.1%), and minute quantities of antifoam agents, proteins, antioxidants, fragrances, antimicrobials, and sunscreens. If a propellant is included, 30 percent DME is preferred, although hydrocarbon or DME/hydrocarbon mixes are also possible.

The following base hairspray composition is provided in the patent: water (90.018%), Eastman AQ-38S (5.775%), Luviskol VA 73W (3.45%), Triton X-100 (0.300%), polyvinylpyrrolidone (K-90) (0.150%), fragrance (0.150%), Dow Corning 190 SU (0.100%), cetearyl octanoate (0.030%) triethanolamine (0.025%), DL-panthenol (0.001%), and vitamin E acetate (0.001%). Seven hairspray compositions were tested for rinsability and hair hold capability. All seven formulations contained the same base composition described above except that each formulation contained a different concentration ratio of the Eastman AQ-38S resin and Luviskol VA 73W copolymer. Based on the evaluations, it was found that the formulation having a 77 resin:23 copolymer ratio exhibited the optimum performance for the two characteristics tested.

The next two aerosol/pump patents are held by Eastman Kodak Company and Helene Curtis, Incorporated. The Eastman Kodak Company patent (Table 3, Reference 6) is titled "Hair Spray Formulations Containing A Polyethylene Glycol Ester of Caprylic an Capric Acids" and relates to hairspray compositions which eliminate flaking. The compositions are based on (1) a sulfonate-containing, water-dispersible or water-dissipatable, linear polyester having a glass retention temperature (Tg) of 33-60 degrees C (1-10%), (2) a polyethylene glycol ester of a mixture of caprylic and capric acids , (3) an alpha-hydroxy carboxylic acid having 2 to 6 carbon atoms, (4) water or a hydroalcoholic mixture (46-94%), and (5) DME (30-35%), or hydrocarbon propellant (3-40%) for aerosol applications. Of the 14 examples of prepared hairspray compositions, it was stated that after applying two aerosol and two pump compositions on hair, no flaking was observed. It was also stated that these compositions provided the hair with good hold properties without a tacky or sticky feel. These compositions contained 55.47 percent water. The propellants used in the two aerosol compositions were DME or an isobutane/propane mixture. After applying the remaining ten prepared hairspray compositions on hair, it was observed that there was either flaking or a tacky or sticky feel.

The aerosol/pump patent (Table 3, Reference #9) held by Helene Curtis, Incorporated (HC) is titled "Aqueous Hair Styling Aid." This patent relates to an aqueous composition which consists of a water-soluble or water-dispersible fixative resin that is a linear homopolymer or random copolymer including a monomer selected from the group consisting

of a vinyl monomer and an acrylate monomer (2-40%), a water-soluble electrolyte selected from the group consisting of various salts, alkali metals, and alkaline earth metals in an amount of at least about 0.001N, water (30-90%), alcohol (0-30%), and for aerosol applications, a propellant (30-50%). Other ingredients may include emulsifiers, preservatives, emulsifiers/conditioners, thickeners and viscosity modifiers, pH adjusting agents, hair oxidizing agents, hair reducing agents, chelating agents, and polymer plasticizing agents in amounts of 0.5-5.0 percent. Additional ingredients may be used such as plasticizers, silicones, emollients, lubricants, penetrants, dyes, tints, and perfumes in amounts of 0.75-1.0 percent.

In the HC patent, numerous examples of compounds are listed which can be used to form the fixative resin to provide the "best aesthetics and spray delivery." The patent also lists numerous examples of salt compounds which may be used as the electrolyte. According to the patent, the electrolyte is used for the purpose of lowering the viscosity of the composition to achieve a higher percentage of polymer in the composition and improve the aesthetics and ease of spraying from aerosol and pump sprays. It does this by preventing the formation of aggregates thereby prolonging the stability of the formulation. The electrolyte reduces the viscosity of the composition by eliminating intermolecular and intramolecular polymer interactions. While no specific examples of prepared compositions are provided in the patent, it is claimed that the compositions can provide the hair with a particular shape or configuration.

The remaining five aerosol/pump patents are assigned to ISP Investments, Incorporated (ISP). The first aerosol/pump (Table 3, Reference #10) held by ISP is titled "Clear Hair Spray Composition Capable of Forming Low Tack Films Which Dry Rapidly." The composition may consist of a fixative resin that is a linear homopolymer of random copolymer including a monomer selected from the group consisting of a vinyl monomer and an acrylate monomer (2-9%), hydrolyzed crosslinked maleic anhydride C1-C5 alkyl vinyl ether copolymer (0.08-0.35%), water (12-42%), and alcohol (55-80%). In this patent, one example is provided for an 80 percent VOC hairspray composition with three varying amounts of hydrolyzed crosslinked copolymer therein. The three variations were compared against a control and evaluated for dry time and tack. The results in the patent indicated that the presence of the hydrolyzed crosslinked polymer in all three variations of the hairspray composition substantially reduced the total drying time and tack-free time as compared to the control without the polymer component. No additional test information is provided. Although the patent provides information for a composition with a 55 percent alcohol content, no other examples of hairspray compositions are given.

The second ISP aerosol/pump patent (Table 3, Reference #11) is titled "Hair Spray Resin Composition." This patent offers a hairspray composition which has a resin comprised of a terpolymer consisting essentially of (1) a vinyl ester, preferably vinyl acetate, (2) a water-soluble or water-miscible alkyl maleate half-ester, preferably mono-N-butyl maleate, and (3) an N-substituted acrylamide, preferably N-t-butyl acrylamide, N-t-octyl acrylamide, or N-(1-(2-pyrrolidonyl)ethyl)acrylamide, in a molar ratio of 1:0.6-0.8:0.08-0.12, respectively, and having a relative viscosity of about 1.2-2.0. The terpolymer resins can be produced either by a suspension or solution polymerization process. When used as the sole active hair holding agent in the formulation, the preferred terpolymer concentration is 1.0-5.0 percent in aerosols

and 4-12 percent in pump sprays. While the patent suggests a composition range for a 55 percent VOC formulation (4-5% terpolymer, 45-55% alcohol, 40-50% water, and 30-70% neutralized), no specific sample compositions are provided.

The patent (Table 3, Reference #12) titled "Hair Spray Composition Containing Water Soluble Alkylated PVP Copolymers as Hair Fixative Therein" is the third aerosol/pump patent held by ISP. According to the patent, the hairspray composition is capable of delivering a fine finishing mist at a high resin solids level. It is claimed to be moisture resistant and to provide a stiff resin film having excellent hair holding power, with relatively low VOCs. The composition incorporates a water-soluble or dispersible alkylated polyvinylpyrrolidone (PVP) copolymer powders having a predetermined blend of two monomer components, one being PVP having a defined molecular weight and the other an alkylene having a selected number of carbon atoms. A suggested composition range for pumps is 0.5-10 percent water-soluble or dispersible alkylated PVP copolymer powder, 10-99 percent water, and 0-60 percent alcohol. For an aerosol composition, a suggested range for the ingredients may be 3-8 percent water-soluble or dispersible alkylated PVP copolymer powder, 50-95 percent water, 5-50 percent ethanol, and 35 percent propellant. A preferred copolymer resin for use in the hairspray composition is Ganex 904 from ISP.

In the patent, six compositions were prepared and tested for effectiveness as a pump hairspray. The six samples contained the following ingredients and composition ranges: Ganex 904 (3-8%), ethanol (0-47.5%), and water (47.5-95%). According to the patent, the formulations were one-phase systems and were observed to develop spray patterns which were fine, broad, and dry. Also, the curl retention properties at 90 percent relative humidity and 80 degrees F were excellent even after 90 minutes.

The fourth ISP aerosol/pump patent (Table 3, Reference #15) is titled "High Water Content Hair Spray Composition" and offers an aqueous or hydroalcoholic hairspray composition which contains a surface active agent. The surface active agent or agents substantially decreases the surface or interfacial tension of the hydroalcoholic phase of the composition during use. For the waterbased composition, the surface tension is decreased along the length of the hair shaft enhancing its spreading tendencies so that substantially no droplets can form upon application of the composition on the hair. Preferably, the surface active agent is an N-alkyl substituted lactam, having from 4-22 carbon atoms, linearly or branched, such as N-octyl pyrrolidone. The preferred composition weight ranges for pump sprays are as follows: resin (4-6%), water (at least 39%), alcohol (55% or less alcohol), surface active agent (0.2-0.4%), base (0.2%). The aerosol composition may be a concentrate (pump composition, 50-80%) and a suitable propellant (20-50%). The patent refers to resins that are described in 20 other U.S. patents which are suitable candidates for use therein, with the preferred hair fixative resins being alkyl vinyl ether/maleic anhydride half-ester resins (Gantrez ES copolymers) or vinyl acetate/monobutyl maleate/isobornyl acrylate resins (Advantage CP terpolymers). An organic base such as aminomethylpropanol is included in the composition to further solubilize the resin component.

Three nonaerosol 80 percent VOC hairspray compositions were prepared and tested for curl retention, drying time and curl droop by the standard test procedures manner of the art. According to the patent, the composition which contains the surface active lactam

exhibited substantially improved curl retention, lower drying times, and more effective curl droop than the composition which contained a surface active agent which does not substantially reduce the surface tension of the water solution, or contained no surface active agent. Through additional testing it was found that the composition containing the surface active lactam exhibited more uniform, fine spray patterns, less tackiness, less comb drag, more luster and sheen, and a cleaner feel on the hair than the other two compositions. While the patent allows for the preparation of 55 percent VOC compositions, no specific examples are provided.

The final aerosol/pump patent (Table 3, Reference #17) held by ISP is titled "Hair Spray Resin Composition." and should not be confused with the other ISP aerosol/pump patent of the same title in Table 3, Reference #11. The hairspray composition in this invention is said to provide a fine finishing mist at a high resin solids level, is substantially moisture resistant, provide a stiff resin film having excellent hair holding power, and have a relatively low concentration of VOCs. The composition attains these characteristics by including a predetermined blend of at least two hairspray resins, a relatively high molecular weight resin and a relatively low molecular weight resin. The low molecular weight resin is present in the composition in a substantially greater proportion than the higher molecular weight resin. The preferred form of the high molecular weight resin is a terpolymer derived from the polymerization of vinyl caprolactam, vinyl pyrrolidone and an ammonium derivative monomer having from 6-12 carbon atoms selected from the group consisting of dialkyl dialkenyl ammonium halide and a dialkylamino alkyl acrylate or methacrylate, having a molecular weight of about 150,000, and the preferred form of the low molecular weight resin is polyvinylpyrrolidone (PVP) having molecular weight of about 15,000, wherein the total weight of both resins is about 13 percent of the hairspray composition.

The optimum pump hairspray composition suggested in the patent is as follows: high molecular weight resin (5%), low molecular weight resin (8%), water (37%), and alcohol (50%). The optimum aerosol hairspray composition suggested is 65 percent concentrate and 35 percent propellant, with the suitable propellants being DME, hydrocarbons, or compressed gases. In this case, the VOC content of the aerosol hairsprays may be higher than 55 percent. There are several high molecular weight resins which are considered suitable for the composition. They are Gaffix VC-713, Gantrez SP-215, Gantrez ES-225, Gantrez ES-425, and Resin 1212, which are all available from GAF Chemicals.

In the patent, three hairspray compositions were prepared and tested for effectiveness as a pump spray. Each composition contained a different high molecular weight resin, the same low molecular weight resin, and varying amounts of aminomethylpropanol, ethanol, and water. The VOC content of these hairspray compositions ranged from 45-60 percent. According to the patent, all three hairspray compositions were one-phase systems whose spray patterns were fine, broad and dry. As comparative examples, the low molecular weight resin in each of the three hairspray compositions was replaced with higher molecular weight resins and tested for effectiveness as a pump spray. The patent stated that these formulations exhibited poor viscosity and gave very narrow, streamy and wet spray patterns.

C. Technical Literature Summary

Summary of Findings:

An extensive review of the technical literature indicates that, while there are challenges associated with formulating a 55 percent VOC hairspray, manufacturers and raw material suppliers are actively developing solutions and in some cases have already developed complying formulations. The challenges are as follows:

Pumps:

Technical Issues - Formulation of a hairspray with 45 percent water is challenging, but it appears that resin, hairspray, and valve manufacturers have already addressed many of the challenges. The technical information indicates that it is possible to formulate 55 percent pumps and, in fact, there is at least one pump that is currently commercially available that meets the 55 percent VOC standard. This example is the Clairol "Final Net" pump at which contains no VOCs (Appendix B, Clairol Product Advertisement; Wurdinger, 1995).

Costs - The resins for hydroalcoholic systems may be more expensive than the traditional resin, but as water will replace the more expensive organic solvents, the cost impacts may not be significant.

Aerosols:

Technical issues - It is possible to formulate an anhydrous 55 percent VOC aerosol at this time that has performance characteristics essentially equivalent to the traditional high-VOC hairspray, using the non-VOC propellant HFC-152a, ethanol, and resin. Products formulated in this way have the advantages of the traditional anhydrous hairsprays, including quick drying times, good flow and hair bonding properties, container stability, and low initial curl droop. However, because of the current high cost of HFC-152a, manufacturers and raw materials suppliers are investigating the use of systems that minimize the amounts of HFC-152a required. These systems use various combinations of HFC-152a, dimethyl ether (DME), hydrocarbon propellants, ethanol, and water, and are more technically challenging to formulate than the simple anhydrous formula mentioned previously. The technical literature indicates, however, that the aerosol products incorporating water into their formulations can presently closely approach the performance of the traditional anhydrous and 80 percent products.

Costs - The propellant HFC-152a is expensive relative to hydrocarbon propellants, as, at $1.95/lb., it costs about 8 times that of hydrocarbon propellants. However, as noted above, research and development efforts have gone into formulations that allow the minimization of the amount of HFC-152 necessary in the formulation, decreasing costs to the manufacturers (see Chapter V, Section F, "Estimate of 55 Percent Aerosol Hairspray Materials Cost").

Findings:

A thorough analysis of the technical information was performed. This included a review of the trade journals, including Cosmetics and Toiletries Magazine, Spray Technology and Marketing, Drug and Cosmetic Industry, and technical books and information including "Chemical and Physical Behavior of Human of Hair," and information from DuPont regarding the Dymel propellants ("DuPont Dymel Aerosol Propellants). Additionally, a sales brochure and advertisements posted in the technical journals and other sources are cited, touting various resins' usefulness in formulating 55 percent (and lower) VOC hairsprays, and the properties of a presently available zero VOC product (See Appendix B). Eleven technical articles were found which directly address the formulating challenges/issues associated with the upcoming 55 percent VOC standard for hairsprays, and discussed solutions achieved to date. These articles were published between 1992 and 1995, with the majority published in 1995.

How do manufacturers and raw materials suppliers propose to decrease the VOC content of hairsprays? There are six general approaches to meeting the 55 percent VOC standard (Russo, 1995; HBA Global Expo, 1994).

Pumps:
1) Replace VOC (generally ethanol) with water
2) Qualify for an innovative product exemption

Aerosols:
1) Include water in aerosols by using DME (which is water-miscible) as a propellant
2) Replace the hydrocarbon propellant with HFC-152a
3) Use various HFC-152a/DME/hydrocarbon/water combinations
4) Qualify for an innovative product exemption

Generally, the technical articles begin by outlining the challenges associated with the 55 percent VOC standard. To summarize, many of the currently used polymers work well in products containing little or no water, and that is how hairsprays were generally formulated before VOC content was an issue (Schill et al., 1995; Price, 1995). The simplest and least expensive way to decrease VOCs from these traditional anhydrous hairsprays, containing between 91 and 97 percent VOCs, is to replace either the ethanol or the propellant with water. However, unless appropriate steps are taken to address the limitations of the traditional formulations, inclusion of water in previously anhydrous systems can have some negative packaging and performance impacts (Price, 1995). As also described by the CTFA Hairspray Group, issues that can be associated with directly replacing solvents with water include the potential for solvent/propellant incompatibility, possible can corrosion, chemical breakdown of the resin, increased dry time and initial curl droop, reduced humidity resistance, and a tacky feel during the drying process. Additional water can also cause increased viscosity and surface tension, resulting in sprays that are coarser and wetter, which further aggravates the dry time and initial curl droop problems mentioned previously. Following is a summary of the technical literature detailing the steps hairspray manufacturers and raw material suppliers have taken to address these issues.

Pumps: Option 1 (Reformulate to allow replacement of the VOCs-generally ethanol-with water):

Resin manufacturers have developed resins that address many of the issues described above, in regard to increasing the water concentration in pump products. One example is the "Acudyne ™ 255" polymer developed by Rohm and Haas (Schill, 1995). Among its properties it is described as follows: "Its key feature was its effectiveness in pump and aerosol hairsprays containing as low as 55 percent volatile organic compound (VOC)." This resin is soluble in solutions containing up to 65 percent water, and is chemically stable in these solutions. After neutralization, its tensile strength, film flexibility and hygroscopic properties resulted in "excellent high humidity curl retention." Also, "the polymer did not form any strong associations with water, leading to quick dry times and low if any tack on the hair." In regard to specific performance properties, curl retention of a 55 percent VOC pump product formulated with this resin compared favorably to a commercial 80 percent VOC pump hairspray. The drying time profile of the 55 percent pump product was very similar to that of the 80 percent pump. Dry time is characterized by three stages: the "wet" stage, the "tacky" stage, and the "dry" stage. Both were dry in under 50 seconds. The 55 percent product was dry in about 48 seconds, whereas the 80 percent pump was dry in about 43 seconds. The wet phase was about 1 second longer and the tacky phase was about 3 seconds longer in the 55 percent product. Curl droop was slightly greater than that of the 80 percent pump, with percent curl retention in the 55 percent product being about 88 percent and in the 80 percent pump being about 90 percent. The anhydrous product retained about 95 percent of the curl. In order to obtain curl retention nearly equivalent to that of the 80 percent pump, it was necessary to use a seven percent concentration of polymer, rather than a 5 percent resin concentration used in the 80 percent VOC product. In summary, Rohm and Haas believes that the Acudyne 255 polymer performed well in a 55 percent formulation and addresses many of the critical performance issues associated with low-VOC products (Schill, 1995).

A new resin based on aqueous dispersion technology has been developed by Amerchol Corporation (Pavlichko, 1995; Amerchol Corporation Product Advertisement). This resin, described as an aqueous dispersion resin (ADR) in the technical article and Amerhold DR-25 in the product advertisement, "...affords the research chemist the flexibility to develop highly functional hair-spray systems that also meet future VOC guidelines (Pavlichko, 1995)." Many of the resins currently available interact very strongly with water in solution (Schill, et al., 1995). Therefore, the viscosity of these polymers can become very high when dissolved in solutions containing 40 to 70 percent water (Hinz, 1995). This aqueous dispersion technology allows the small, solid resin polymers particles to be suspended in water without settling out. These particles are coated with surfactants, which act to stabilize the emulsion by prevent the resin particles from agglomerating. This results in a low viscosity aqueous phase, which allows higher polymer concentrations and resins with higher molecular weights to be used. This resin can be used in aerosol and pump hairsprays. Studies show that the performance of this resin when formulated into a 55 percent VOC pump (seven percent resin and 55 percent ethanol), is superior in regard to curl retention under very humid conditions (90 percent relative humidity), when compared to two 80 percent VOC pump products that are currently available, one in the retail market and one in the salon market. Even under this extreme condition it shows approximately a 90 percent curl retention after one hour in this new resin, whereas the other two products showed between 80 and 85 percent curl retention.

A second study (Amerchol Corp. Product Advertisement) showed that "a 55% VOC system containing 6% Amerhold DR-25 offers superior curl retention even when compared to an 80% VOC solution polymer system." Curl retention after one hour for the 55 percent product was 92 percent, and at 4 hours was 83 percent, while the one and four hour curl retention for the 80 percent products were 82 percent and 77 percent, respectively.

The Amerchol resin was also salon performance tested in a 55 percent VOC pump form (with small amounts of additional resins added to optimize the system to a more "finished" product) against an 80 percent ethanol retail pump product using a "half-head" method. Cosmeticians graded the two products for drying time (including tack), stiffness, curl retention, and rinsability. In regard to dry time, performance was equivalent, with both well within acceptable drying times for pumps, with the 80 percent product having a "slight advantage." The cosmeticians actually preferred the test product because of lower perceived tack during and after drying. The two products could not be differentiated in regard to stiffness and rinsability. The test product was judged to be superior in regard to curl retention. Amerchol summarizes the results by saying that this resin "yield[s] stiff, flexible films that contribute to excellent high-humidity curl retention in both aerosol and non-aerosol hair-spray formulations..." and "As a result of this new acrylates copolymer technology, hairspray systems can now be formulated to meet consumer desires while addressing the proposed regulations regarding VOC levels (Pavlichko, 1995)."

Clairol's Roy Blank, vice-president of hair care, states that "We've developed 55 percent products that have tested well...Final Net contains no alcohol and has gained consumer acceptance. The solution is really a combination of different systems and resins." He does note that Clairol has had more success with the aerosols than the pumps, but indicates that consumers will become accustomed to a longer dry-time, although professionals will continue to value a short dry-time (Wurdinger, 1995).

Eastman Chemical Company AQ polymers are advertised to speed up apparent dry time, have excellent resistance to humid conditions, allow production of formulations down to zero VOC in pump or aerosol (Appendix B, Eastman Chemical Company Advertisement). These polymers will be discussed further under the "Raw Material Contact Summary."

Pumps - Option 2 (innovative product exemption):

According to Dr. Jack Guth of National Starch and Chemical and John Leuszler of DuPont, it is possible to implement a strategy using a higher solids concentration, coupled with a lower delivery rate, to formulate an innovative product which matches the performance of the anhydrous product, yet results in less emissions per use (HBA Global Expo, 1994).

Aerosols: Option 1 (Include water by using DME, a water miscible propellant):

Rohm and Haas notes, of the Acudyne 255 polymer discussed previously and found to perform very well in water-containing pump formulations (Schill et al., 1995), that "We found that 55 percent VOC aerosol formulations could also be easily prepared using the propellants DME, HFC-152a, or a combination of both." Therefore, it can be used in the pump formulations described above, or as aerosol formulations in both anhydrous and hydrous

solutions.

National Starch and Chemical's Dr. Jack Guth also notes that the performance of an 80 percent VOC aerosol can match the performance of an anhydrous system if new resins are used, and at 55 percent VOC, performance can approach anhydrous (HBA Global Expo, 1994). Using an existing resin, he notes that dry time for an anhydrous product is about 5.3 seconds, while the 80 percent product had a dry time of 9.5 seconds, and the 55 percent product had a dry time of 13.2 seconds. However, he does indicate that polymer modification and changes in resin concentration can ameliorate the negative effects. For example, by modifying the resin to reduce polymer viscosity, spray aesthetics can be improved, and by increasing the hydrophobicity of the resin, drying time is reduced, as is initial curl droop, and humidity resistance is increased. Initial curl droop is also dependent upon the type and amount of resin used. Increasing polymer concentration can ameliorate initial curl droop. For example, an anhydrous product shows about 93 percent curl retention in the initial curl droop test (which is matched by a high solids 80 percent product); however, the high solids 55 percent product shows about a 90 percent curl retention in the initial curl droop test. Humidity resistance of the 55 percent product matches that of an anhydrous aerosol in this study. Again, a higher resin concentration (6 percent rather than 4 percent), is required to obtain equivalent results (HBA Global Expo, 1994).

The Amerchol resin described previously, based on aqueous dispersion technology (Pavlichko, 1995; Amerchol Corporation Product Advertisement) and shown to perform very well in water-containing pump systems, can also be used to formulate aerosol hairsprays. This resin can be incorporated into DME/water-containing aerosol hairsprays, as Amerchol's initial work shows the resin to "be completely compatible with DME." In aerosol as well as non-aerosol systems, this resin results in excellent high-humidity curl retention.

National Starch and Chemical also has a Lovocryl-47 resin which is specifically designed for low-VOC formulas (Russo, 1995). Here it is indicated that this resin, in a product with high solids and DME as propellant, is a viable approach to formulating a high solids 55 percent VOC aerosol. In this product, "the effects of the water are mitigated and the style of the hair is retained." In a study comparing the initial curl droop of an aerosol high solids 55 percent hairspray with a 95 percent VOC anhydrous product, the high solids 55 percent product performed well, with the percent curl retention in the initial curl droop test of about 86 percent, compared to a percent curl retention in the initial curl droop test of about 90 percent with the anhydrous, high-VOC product. The hairspray designed as an innovative product at 55 percent VOC actually outperformed all the above, with percent curl retention in the initial curl droop test of approximately 92 percent. However, another approach presented by National Starch and Chemical involves the formulation of a two-phase water-based aerosol hairspray including DME at concentrations that exceed its solubility in water. This is done because "higher levels of propellant in an aerosol spray will lead to better break-up of the concentrate and a drier spray." The benefits, in addition to that just noted, include a lower concentrate viscosity, which will result in better atomization, a better spray pattern, and quicker drying. It is also noted that the spray dries in a clear film. The product described in the article actually has a VOC content of 45 percent. They note that "...formulation of VOC systems 55% or less, as well as alcohol-free claims, are feasible with this technique. The system is versatile since a variety of resins, solids levels, and propellant levels can be used.

Additional surfactants can be added to further stabilize the emulsion." Russo summarizes by noting that "formulating with a high solids, propellant 152a or a two phase alcohol-free system offer different avenues for the formulator."

Eastman Chemical Company AQ polymers are advertised to, among other claims, speed up apparent dry time, have excellent resistance to humid conditions, allow production of formulations down to zero VOC in pump or aerosol (Appendix B, Eastman Chemical Company Advertisement).

Aerosols - Option 2 (Replace the hydrocarbon propellants with HFC-152a):

DuPont has tested a 55 percent VOC aerosol hairspray (containing 55 percent alcohol and 35 percent HFC-152a) for curl retention, and shown it to be either equivalent or superior to commercial anhydrous sprays in regard to percent curl retention at ten minutes using a protocol from ISP. The vapor pressure was found to be well within the acceptable range for aerosol hairsprays. DuPont also notes that "One of the characteristic weak points of a water-based spray is initial droop, seen a few moments after the styled has been sprayed. Often the curl retention will be identical to, if not better than, an anhydrous formulation but the first few performance measurements are very poor. For this reason, a key data point in the studies has been a 10-minute curl retention reading (Boulden, 1992)."

As noted previously, National Starch and Chemical also has a Lovocryl-47 resin which is specifically designed for low-VOC formulas (Russo, 1995). They indicate that this resin can also be formulated to allow the incorporation of HFC-152a, resulting in an anhydrous product. Benefits of formulating an anhydrous spray such as this include "quick drying time, ideal flow properties for bonding of the hair, elimination of can stability problems due to water, and little initial curl droop."

The Rohm and Haas Acudyne 255 polymer resin could also be easily formulated into an aerosol product containing HFC-152a alone, or an HFC-152a/DME combination (Schill, 1995).

Aerosols - Option 3 (Use various HFC-152a/DME/hydrocarbon/water combinations):

By using various combinations of DME/HFC-152a/water it is possible to adjust the hairspray to meet performance and cost specifications. For example, "by adjusting the HFC/DME ratio, the water content, pressure and cost can be adjusted. In fact, it is possible to formulate a product containing from 0 to 41 percent water using this strategy (Strobach, 1993). There are several published formularies for aerosol products with HFC-152a concentrations of less than 10 percent, substantially decreasing the cost of reformulation. DuPont has tested these formularies for curl retention, which is a critical performance parameter, and found that these products perform as well as the "traditional" anhydrous aerosol hairsprays (Boulden, 1992). For example, one formulation (29% water, 20.4% DME, and 9.6% HFC-152a) showed ten minute curl retention of 89 percent, compared to two commercial anhydrous products with curl retentions of 88 percent and 93 percent. The one hour curl retention was 75 percent for the 55 percent VOC hairspray, with 71 percent and 79 percent for the two commercial anhydrous products (Boulden, 1992). DuPont is also

investigating the use of HFC-152a/DME/hydrocarbon formulations which include only a small amount of water (DuPont, 1/24/96). This is a fairly new development, so there aren't any formularies yet available. However, this should give manufacturers even more options when formulating aerosol 55 percent VOC hairsprays.

DuPont notes that an approach involving the blending of HFC-152a, dimethyl ether, and hydrocarbons may be the best strategy, along with variations in resin concentration and delivery rate (HBA Global Expo, 1994). "By utilizing all three strategies, an acceptable product that could meet the future limits should be attainable (DuPont, 1996)." Additionally, DME/HFC-152a/hydrocarbon blends are already available from Aeropres Corporation, Diversified CPC International, and Technical Propellants (HBA Global Expo, 1994). DuPont also notes that the cost to make HFC-152a will decrease with their new technology and this, combined with competitive pressure, should result in lower prices in the near future (DuPont, 1996).

DuPont's Louisville plant has doubled capacity and a second plant is under construction at Corpus Christi, Texas, and is scheduled for late 1996 startup, in time to support national distribution of reduced VOC personal care products. Furthermore, should additional VOC regulations be implemented and HFC-152a demand increase significantly as a result, the plant has the ability to expand rapidly (Spray Technology and Marketing, 1995; DuPont, 1996).

Aerosols - Option 4 (Qualify for an innovative product exemption):

Anhydrous innovative 55 percent VOC aerosols can be formulated that are equivalent to traditional high-VOC anhydrous systems according to National Starch and Chemical (HBA Global Expo, 1994). National Starch and Chemical compared various products, including an anhydrous high-VOC aerosol product with an "innovative" 55 percent VOC aerosol product. This innovative 55 percent product uses a DME/hydrocarbon-propelled high solids formulary which contains only 8 percent water. They found that the innovative product actually performed better than the 95 percent anhydrous product in terms of percent curl retention (Russo, 1995).

Resins for Low-VOC Hairspray Products:

There are numerous resins available for formulating low-VOC hairsprays. Several have been described previously, but following is a short summary (Price, 1995):

Trade Name*	**Supplier**
Ultrahold-8	BASF
Amerhold DR-25	**Amerchol**
Acudyne 255	**Rohm and Haas**
Diahold	Sandoz
Eastman AQ Polymer	**Eastman Chemical**
Diaformer	Sandoz
Amphomer, Lovocryl-47	**National Starch and Chemical**
Resyn 28-2930	National Starch and Chemical
Advantage CP	ISP
Gaffix VC-713	ISP

* Those resins and suppliers shown in bold are discussed in the technical review.

Other components that can be modified to aid in the formulation of low-VOC hairsprays:

There are now valves available which help obtain uniform fine sprays over a much wider range of product viscosity, solids concentration and solution surface tension. Additionally, other pressurizing alternatives to hydrocarbon propellants exist. Examples include the "Exxel Atmos System" by Exxel Container, the "Eurospray" bottle by Inter Airspray AB, the "Advanced Barrier System" by Advanced Monobloc, and "Pepcap" by Belgium Spray (Price, 1995).

Corrosion Issues:

DME/water-based formulations can be corrosive to tinplate and aluminum aerosol containers. The use of corrosion inhibitors may therefore be required, along with extensive storage tests (Strobach, 1993).

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D. Manufacturer Contact Summary

Summary of Findings:

For the purposes of this section, the ARB staff did not contact any of the hairspray manufacturers which attended the CTFA Hairspray Group meeting in October 1995. Since the information provided by these companies is discussed in detail elsewhere in this report (see section A, chapter V "Findings"), the purpose of this section is to discuss the efforts of hairspray manufacturers who are not part of the CTFA Hairspray Group.

Out of the 76 hairspray manufacturers in the ARB registration database, 30 firms were contacted (39 percent of the total; seven of the companies contacted are either located in California or have a local office/plant).Their opinions on the state-of-the-art and developing technologies for meeting the 55 percent VOC standard varied widely. Some manufacturers believe the standard is nearly impossible to achieve and others were confident they can meet the standard by 1998. Overall, the opinions of most manufacturers contacted fell between these two extremes. Key research and development efforts appear to emphasize refinement of current prototypical formulations to satisfactorily meet performance criteria in pump spray and aerosol products for the mid- to low-end household retail market. Little concern was expressed regarding the industry's technological/commercial ability to meet the 55 percent standard for the professional salon market; the high profit margin for this market is expected to help absorb or offset the higher cost of using HFC-152a as a propellant.

The opinions/statements provided in the telephone survey yielded the following information: (1) three companies currently sell 0 percent VOC pump spray products which they claim are doing relatively well in the market; (2) three manufacturers expressed confidence in their ability to have complying pump or aerosol formulations within the next 12-15 months or in time to meet the standard; (3) three companies believe the 55 percent standard is achievable and expressed guarded optimism in the results of their work with resin suppliers to develop satisfactory formulations; (4) twenty-two companies stated it is too early to determine whether the 55 percent is achievable by 1998, but they are working diligently with the resin suppliers or contract fillers; and (5) two companies have little ongoing R&D efforts and will be relying heavily on complying formulations to be provided by the resin suppliers or contract fillers.

Findings:

Because each manufacturer's research and development efforts are unique and closely guarded from competitors, the telephone discussions yielded a wide range of opinions regarding the state-the-art and reasonably expected developments in 55 percent VOC complying hairspray formulations. Several manufacturers are not conducting their own research; rather, they are relying on contract fillers to provide complying product formulations by the standard's effective date. Other manufacturers are conducting intensive research with the resin suppliers to develop their own high-water compatible resins.

While the opinions given ranged from "definitely can/will" to "definitely cannot," most manufacturers contacted did not state that the 55 percent standard is impossible to achieve by 1998; rather, they indicated that it's too early at this point to determine whether their company can meet the standard in time. In general, these marketers are relying heavily on research by the major resin suppliers (see following discussion on "Raw Material Suppliers"). Various prototype formulations have been provided by the resin suppliers and research into refining these and developing other complying formulations is proceeding. For these efforts, most of the research is being applied to further refine one or more performance characteristics of the prototypes (e.g., curl droop, dry time, viscosity). Although several manufacturers expressed dissatisfaction with current prototypical formulations, other manufacturers expressed confidence in either their ability to develop complying formulations or the ability of the resin suppliers to develop fully water-compatible, high performing resin systems before the 1998 compliance date.

According to the manufacturer contacts, the main research efforts appear to be focused on developing satisfactorily performing pump and aerosol hairspray formulations for the household retail market; less research emphasis appears to be placed on developing formulations for the professional salon market. This is not altogether surprising, since various high performance aerosol formulations using HFC-152a to some degree have been published for several years. Because of the high profit margins in professional salon products, most manufacturers contacted expressed little concern that complying formulations for the salon market can be developed, even with the higher cost of HFC-152a. On the other hand, the higher cost of HFC-152a (currently at $1.95/pound vs. $0.25/pound for n-butane and $0.40/pound for DME) is expected to drive more research into high water, DME-based formulations for the low-end to mid-range retail products.

In addition to the findings discussed previously, other specific highlights from the telephone survey of manufacturers/marketers are presented as follows:

- Three companies stated that they have been selling alcohol-free, 0 percent VOC hairspray (pumps) for several years; these products have been relatively well-received.

- Three companies indicated their current efforts should result in 55 percent VOC candidate products (both aerosol and pump spray) within the next 12-15 months; these companies do not anticipate significant problems in attaining this goal;

- Several manufacturers indicated that a key to successful marketing of 55 percent VOC hairsprays may be to adequately inform consumers of the differences and strengths between 55 percent VOC products and current 80 percent products (e.g., somewhat longer drying times but higher solids content to provide more product per container at lower cost);

- Several manufacturers indicated that the perceived differences between a 55 percent product and an 80 percent product are more noticeable in the

professional salon market than they are in the retail market; the performances differences, if any, become negligible if HFC-152a is used in the professional market, which is not as sensitive as the retail market to potential cost increases from using HFC-152a.

E. Raw Material Supplier Contact Summary

Summary of Findings:

From discussions with one propellant, two actuator, and six resin suppliers, it appears the 55 percent VOC hairspray standard is technologically feasible by the January 1, 1998 effective date; however, some of the formulation options have commercial feasibility concerns. All those involved in the pump and aerosol reformulation process agree that the development of efficacious 55 percent VOC products will be the result of a combined effort between product manufacturers, resin manufacturers, propellant suppliers (aerosol only), and actuator suppliers. Many resin suppliers have already developed working relationships with other types of suppliers and have developed successful 55 percent VOC formulations. For instance, most resin suppliers are working with actuator suppliers to optimize the spray characteristics for their resins unique qualities. A summary of our findings for the aerosol and pump forms is discussed separately below.

Aerosol Formulations:

Currently, aerosol formulators have three reformulation paths to explore when developing 55 percent VOC aerosol hairsprays. These are: (1) replacement of VOC propellant with HFC-152a; (2) developing DME propelled water based formulas; and (3) using a combination of propellants including HFC-152a and minimizing the amount of water added to the formula.

Formulations which replace the VOC propellent with HFC-152a have performance characteristics comparable to 80 percent VOC formulations. However, the cost concerns associated with HFC-152a may cause these formulations to be limited to the professional salon market where the increased production cost can be more readily absorbed. Most resin and product suppliers believe it would not be possible to absorb the production cost increase in products sold in grocery and/or drug stores. Since product manufacturers that sell to this market are concerned with the economic issues associated with HFC-152a, resin manufacturers are diligently working to produce efficacious and affordable prototype formulation options which use DME/water.

The DME/water formulations challenge resin and product manufacturers in the following areas: dry time, initial curl droop, curl retention, viscosity/surface tension, and can corrosion. While some raw material and product manufacturers appear to have adequately addressed most of these issues and claim their 55 percent VOC formulations are efficacious, others are still trying to focus their resin development research and reformulation efforts to resolve these concerns. Due to the uniqueness of each resin, each polymer manufacturer is focusing on issues, specific to their resin and reformulation needs.

Another aerosol formulation option, which will decrease the economic concerns associated with HFC-152a formulations, is minimizing the use of HFC-152a by utilizing a combination of propellants. DuPont is working with a few resin suppliers to develop several prototype propellant formulations which address both, the product manufacturers HFC-152a economic concerns, and the technical concerns experienced with the DME/water

formulations.

The results of DuPont's efforts along with several prototype formulations will be distributed to the product manufacturers and published in early summer.

Pump Formulations

There appears to be consensus among the raw material suppliers that developing an efficacious pump formulation has been more challenging than the efforts of aerosol reformulation, due to fewer reformulation options available for pumps. According to the raw material suppliers contacted, the only realistic reformulation option for pumps is to replace approximately 25 weight percent ethanol (based on a 80 percent VOC formulation) with water. Formulations will contain at least 40 percent water if no other exempt compounds are used. Pump formulations have challenges similar to those of DME/water formulations. Some resin suppliers, however, have addressed these issues and have customers that are selling 0 percent through 55 percent VOC hairsprays with performance characteristics at or near to those characteristics of 80 percent VOC products.

Findings**:**

Amerchol

Amerchol, a company owned by Union Carbide, manufactures resins. They are considered a relatively new source of hairspray resins, since they were not producing resins for the hairspray market prior to the adoption of the consumer product regulation. However, even though they are a new supplier to the hairspray market, they believe they have a unique resin which can be used successfully in 55 percent VOC hairsprays.

Amerchol's resin is latex based and is prepared through an emulsion polymerization process. This results in a resin that is dispersed in the aqueous phase and overcomes many of the problems encountered when formulating aqueous hairsprays with traditional resins that were developed to perform in anhydrous systems. According to Amerchol, some suppliers have modified traditional resins by adding a neutralizer to improve compatibility with aqueous systems. However, in Amerchol's opinion, this decreases the performance of the resin in a hairspray. Amerchol's resin, on the other hand, because it is based on a different technology, can tolerate large amounts of water, improves the drying characteristics of hairsprays formulated with the resin, and imparts good film forming abilities.

Amerchol has developed low VOC hairspray prototype formulas in both pumps and aerosol forms. For pumps, Amerchol has developed a 0 percent VOC prototype formulation and indicate that other pump formulations can be adapted for any amount of water, however the optimum formula results from a 55 percent ethanol (VOC) formulation. For aerosols, Amerchol has prototype formulations which contain as little as 10-15 percent VOC with the optimum formulation being a 55 percent VOC system that uses 40 percent dimethyl ether (DME) propellant and 15 percent ethanol. Amerchol prefers to use DME in the aerosol formulations since it avoids a two phase system that can result when using hydrocarbon propellants and is less costly than HFC-152a.

The prototype formulas developed by Amerchol have good physical characteristics. The viscosity of these prototypes remains low and is not affected by high solid concentrations. They also have good freeze thaw stability due to careful selection of the copolymer molecular weight and use of a surfactant in the formulation. In addition, Amerchol has worked closely with valve suppliers to optimize the packaging system to reduce the problems with clogging and to optimize the spray characteristics of the product.

Regarding the performance characteristics of aerosol and pump prototype formulations using their resin, Amerchol claims overall, the products had excellent curl retention, and quick dry time[1]. In addition, they believe the combability, feel, shine, tackiness and flaking resistance are equivalent to an 80 percent VOC product. Initial curl droop tests were conducted to evaluate and compare Amerchol's 55 percent prototype formulations with 80 percent market leader formulations, and data indicated the results of Amerchol's prototype formulations were within acceptable limits. Curl retention was the key performance parameter and was examined in an environment of 90 percent humidity. The curl retention test was performed to check the hairspray's ability to hold the style through out the day in extreme conditions. In these tests, Amerchol's 55 percent VOC aerosol and pump prototypes performed equivalently to the 80 percent VOC market leaders.

Even though Amerchol is a relatively new to the hairspray resin market, they have been actively marketing their product. To advertise their product and research, they target their promotion efforts to multi-national product manufacturers and also to mid-size companies. Amerchol has also worked to improve the knowledge about their resins among hairspray manufacturers by publishing in both Drug and Cosmetic Industries and Spray Technology last June.

BASF, National Starch and Chemical Company, and International Specialty Products

BASF, National Starch and Chemical Company (National Starch) and International Specialty Products (ISP) are resin suppliers which market and sell hairspray resins to product manufacturers and have done so for several years prior to the introduction of the consumer product regulation. The resins produced by these companies were originally designed for use in anhydrous systems and, to remain in solution, need to be used with neutralizers. These companies created new resins which, they hoped, could be used to produce efficacious 55 percent VOC hairsprays, by modifying their anhydrous resins and/or creating new resins.

These resin suppliers collaborated to present an overall view of their efforts at the October 19, 1995 CTFA meeting with the ARB staff, and believe two reformulation options exist which can be used in developing 55 percent VOC aerosol hairsprays: 1) the use of HFC-152a as a propellant in an anhydrous system or 2) using DME propellant in conjunction with a water based concentrate. Their resins, originally designed for use in ethanol-based systems, perform well in HFC-152a systems, however, they believe that this option will be too

[1] While a common complaint of 55 percent VOC hairsprays is a longer dry time, Amerchol claims that consumers could not determine a difference in dry time between their 55 percent VOC product and an 80 percent VOC formula.

expensive. While they do have patents or patents pending for 55 percent VOC resin formulations using dimethyl ether (DME)/water, they do not believe these patents adequately address industry's efficacy concerns.

Formulations with DME/water still have dry time, resin stability/compatibility, viscosity/surface tension, and can/valve stability concerns which, they believe, are related to the increase in water. According to BASF, ISP, and National Starch, the drying time and initial curl droop are the biggest concerns, because they believe the additonal water increases formula viscosity and surface tension, evaporates slower than current product formulations, weighs the hair down, and breaks the hydrogen bonds necessary for holding a temporary style. One example presented at the October 19, 1995 meeting by Mr. Joseph A. Dallal of ISP, demonstrated the difference between the tack measurements and dry time of both an 80 percent VOC and a 55 percent VOC formulation (data collected instrumentally).

Measurement	80 % VOC	55 % VOC
Dry time	7.83 minutes	10 minutes
Tack measurements above -2.0 Force [G]	4.5 minutes	3.0 minutes
Strongest measurement at (Force[G])	-12.0 -4.2	

BASF, ISP, and National Starch believe the additional water in the formulation impedes film formation, and softens the hairspray resin and hair. This results in less curl retention (hold), less stiffness, and more initial curl droop, thus decreasing the efficacy of the formulation. According to these companies, the viscosity and surface tension, parameters which are crucial in developing suitable spray characteristics, are also affected by the increase in water. By replacing ethanol with water, both the viscosity and surface tension increase which clogs the valve, increases the spray particle size, and produces a less effective spray pattern. The can/valve stability is decreased as well, with corrosion being its main obstacle.

The research breakthrough which will counteract the negative effects of water, still eludes these resin manufacturers which state that it must be elucidated in order for them to achieve the 55% goal. According to these suppliers, .addressing a negative effect which they attribute to the high water content in their prototype formulations results in other negaitve effects. These companies believe the key to developing efficacious 55 percent formulations is to develop new resins with lower molecular weights or to address the conformation issues with the higher molecular resins. The focus of their resin research efforts will be to develop resins with aforementioned specifications. However, they believe this resin development must be integrated with new propellants, valves, and cans to result in an efficacious 55 percent VOC hairspray. They are still doing research in resin and formulation development and are looking into formulations with propellant combinations which they hope will produce affordable and efficacious 55 percent VOC products in the near future.

DuPont

DuPont has indicated that it believes the 55 percent VOC hairspray standard is both technically and economically feasible for aerosols. DuPont manufactures two types of propellant that can be used in hairsprays: HFC-152a and DME. While several companies

produce DME, DuPont is currently the only U.S. supplier of HFC-152a. HFC-152a is a negligibly photochemically reactive VOC and is exempt from regulations. It plays an important role in hairspray reformulation because it can replace the hydrocarbon propellants in current formulations allowing the product to meet the 55 percent VOC standard without further reformulation. While DME is a VOC, its use is beneficial in high water content formulations because of its excellent water solubility and relatively low cost.

The consumer acceptability of HFC-152a reformulation costs appear relative to the type of product being sold. Hairspray product cost factors play a larger role in the drug or grocery store markets than for those products sold in the salon market. Professional salon products, prior to the adoption of the consumer products regulation, cost the consumer between 8 to 18 dollars a can, in comparison to hairspray products selling under two dollars a can. In 1993, after the 80 percent VOC hairspray standard became effective, many salon products exchanged the hydrocarbon propellant with HFC-152a to meet the standard, with the cost of these products relatively unchanged. Current salon products range from 12 to 20 dollars, though the increase in cost to the consumer may not have been driven exclusively by the formulation change. DuPont points out that the manufacturers for professional salon products may once again rely solely on the use of HFC-152a. DuPont recognizes the use of HFC-152a alone may not be an economically viable option for hairspray products selling under two dollars. To address this issue, DuPont is developing formulations which use propellant combinations and should adequately address these "lower price" products. DuPont realizes the reluctance to use HFC-152a is relative to the cost to use the propellant and that minimizing its use requires more research than those products which opt to use HFC-152a alone.

As a supplier to the hairspray industry, DuPont has kept informed of manufacturers efforts to develop low VOC hairspray formulas. Some of the concerns that they have heard raised by industry include:

- the standard is not feasible,
- the cost of HFC-152a is too high, and
- the DME systems do not perform well due to the presence of large amounts of water.

Over the past few years, DuPont has worked to improve the technology available to reformulate low VOC hairsprays by developing prototype 55 percent VOC formulas that use HFC-152a as a propellant or combinations of HFC-152a, DME, and hydrocarbon propellants. DuPont has organized a technical research group to develop formulations specifically for hairsprays and to work with industry to address their concerns. The goal of this work will be to minimize the use of HFC-152a by using a combination of propellants with possible propellant combinations of hydrocarbon A17 and HFC-152a, DME and HFC-152a, and A17, DME and HFC-152a. In addition to propellant optimization, DuPont is working with a variety of resins from four resin suppliers (Rohm and Haas, National Starch and Chemical Company, International Specialty Products, and BASF) to address the potential efficacy shortfalls and to develop a range of formulations. Other current and future outreach efforts include: trade journal articles addressing the use of HFC-152a in hairspray reformulation, classes offered by DuPont explaining propellant options, a technical report explaining the

current technologies to be released to industry in a couple months, and the release of a range of refined prototype hairspray formulations to industry in early summer.

Although these refined formulations minimize the use of HFC-152a, DuPont indicates it is sensitive to the concerns raised by industry regarding the cost of HFC-152a. According to DuPont, the expected increase of competition in the market, the start-up of DuPont's new HFC- 152a manufacturing facility, and that propellant mixtures can be used in 55 percent formulas, all will likely lead to HFC-152a being a more viable and cost-effective option for manufacturers as they develop 55 percent VOC hairspray formulation. Although DuPont is the only manufacturer in the United States, DuPont believes they will have competition within one to two years, since they know of three companies expressing interest in HFC-152a manufacturing. DuPont spent forty to fifty million dollars expanding existing HFC-152a capacity and developing a new lower cost manufacturing route upon which a second plant is being built. The new plant, built primarily for the ARB hairspray regulation, will allow DuPont to competitively price HFC-152a against the new suppliers, and DuPont expects the cost of HFC-152a to decrease. Nonetheless, the cost of manufacturing HFC-152a will likely continue to be higher than the manufacturing costs of hydrocarbon propellants.

DuPont points out that product manufacturers will not incur any additional can or filling costs when reformulating with HFC-152a. The overall pressure of the hairspray can is within the limits of the currently used 2N, 2P and 2Q cans because the addition of ethanol lowers the pressure of HFC-152a, therefore no additional costs are expected. The filling facilities made changes to accommodate using HFC-152a during tier one of the hairspray standards.

Another cost related concern that has been raised by industry is the supply, or lack of, HFC-152a. While this was a valid concern earlier when the first tier hairspray standards became effective in 1993, DuPont claims that this is no longer an issue. DuPont expects their new HFC- 152a manufacturing plant in Texas to be operational by December 1996, with full capacity reached within a year. If needed, this plant could increase capacity by an additional 40 percent, and this Texas site has room for another facility as well. It appears industry's supply concerns would be more than adequately addressed by the two DuPont manufacturing facilities and if the expected competition comes online in two years.

In summary, DuPont is working diligently to assist manufacturers in developing the 55 percent VOC hairsprays by the 1998 effective date. They have taken several steps to address the supply and cost of HFC-152a and are devoting significant resources to develop feasible low VOC hairspray prototypes that they will share with manufacturers.

Eastman Chemical Company

Eastman Chemical Company (Eastman) manufactures a number of resins for a variety of end use applications. Four of these resins from the "Eastman AQ" water dispersible polyester family are useful in low VOC hairspray applications. The most recent addition to this family, "Eastman AQ 48 Ultra," was designed specifically for 55 percent VOC applications.

The characteristics of Eastman's resins described by the company that would make them useful for low VOC hairspray formulations include low molecular weight, small dispersion particle size, low solution viscosity, and the ability to be adapted to hydrophilic or hydrophobic systems. That these are dispersion polymers would offer a distinct advantage over solution polymers typically used in hairspray formulations. The primary advantage of dispersion polymers is in the significantly smaller particle size. This translates to a smaller aerosol droplet size, which in turn produces faster dry times due to the smaller amount of solvent. The smaller particle size also produces clear formulations. Another unique feature claimed is the adaptability of Eastman's resin for either a hydrophilic or a hydrophobic system, thus allowing the product manufacturers a variety of formulation ranging from totally water-based 0 percent VOC to 55 percent VOC formulations.

Eastman has worked internally to develop a range of formulations that include zero percent VOC pump products, 55 percent VOC aerosol (using DME as the propellant) and 55 percent VOC pump products. In addition, Eastman has worked with valve manufacturers to optimize spray characteristics and evaluate the spray properties of their systems. One customer has made a national product launch for a zero percent VOC pump formulation which uses one of Eastman's resins. Eastman continues to work with customers to develop additional resins for 55 percent VOC formulations to compliment their current product offering. As with their previous development efforts, Eastman focuses on designing resins with the performance attributes required by their customers. These include initial curl droop, curl retention, dry time, viscosity, and aesthetic properties. It is Eastman's intention to have a family of resins to offer their customers a range of formulation options for 55 percent VOC products. Eastman has promoted these materials at various trade meetings and in assorted trade publications. Their past publications include a poster at the Cosmetic, Toiletries, and Fragrance Association, Incorporated (CTFA) show and at the "In-Cosmetics" trade show in Paris. Eastman plans to publish additional articles and presentations to encourage the use of and promote their resins.

Precision Valve

Precision Valve (Precision) manufacturers actuators and delivery systems for both pumps and aerosols for a variety of different industries including the hairspray industry. To aid product manufacturers and resin suppliers in developing efficacious 55 percent VOC hairsprays, Precision works with prototype and refined formulations to optimize the delivery system to provide the best spray characteristics or will provide sample valve systems to product manufacturers for testing in their own labs.

Rohm and Haas

Rohm and Haas is a resin supplier that is relatively new to the hairspray market, and has developed a resin that can be used to produce efficacious 55 percent VOC hairspray formulations. Rohm and Haas believes their resin is one of the best resins in the market for formulating 55 percent VOC hairsprays and their patent, which was submitted approximately one a year ago, is pending approval. Rohm and Haas also believes that due to CARB's consumer product regulation, the hairspray resin market has changed significantly in regards to resin suppliers as well as the technology represented by those companies. According to

Rohm and Haas, three new companies, Amerchol (a subsidiary of Union Carbide), Eastman Chemical, and Rohm and Haas, are now competing with the established market leaders: National Starch (a subsidiary of Unilever) and International Specialty Products (ISP). All three of these new suppliers are large (Fortune 300) polymer producers that have significant resin/polymer offerings and expertise in other film forming applications/markets that have been shifting to lower VOC's outside the Personal Care/Hairspray area. These three new suppliers have brought new technology to the hairspray market including the dispersion type products. Rohm and Haas believes that without the low (55 percent) VOC target, it is doubtful that any of the three new suppliers would have entered the hairspray market at this time.

Rohm and Haas has at least five pump and aerosol formulations which are starting points for their customers. They claim the laboratory performance tests of these 55 percent formulations are equal to 80 percent VOC products which were randomly selected from the shelf, with respect to hold, curl retention, and tack. The dry time of their 55 percent VOC formulations are essentially similar to off-the-shelf 80 percent VOC products with only several seconds difference observed. Rohm and Haas stated the only parameter which has noticeably changed is the initial curl droop. When comparing 55 percent and 80 percent VOC formulations the initial curl droop was 9-12 percent for various 55 percent VOC formulations and around 6 percent for 80 percent VOC products. This would equate to a loss of 1.5 to 2.0 cm for the 55 percent VOC products and 1 cm for the 80 percent VOC products, when based on a 23 cm hair strand curled to a length of 6 cm.

Rohm and Haas, like most resin suppliers, does not have a salon to test their products and their prototype formulation evaluations are based on laboratory tests. Their customers must refine the formulations and perform the salon and consumer evaluations. However, Rohm and Haas has been told by most of their customers that their resin is in the top 2-3 candidates for formulation of 55 percent VOC hairsprays. One product manufacturer stated to Rohm and Haas that the 55 percent VOC formulation they developed was better than their current 80 percent formulation. This product manufacturer used a combination of Rohm & Haas's resin and another manufacturer's resin. In addition, Rohm & Haas believes that several large companies are fairly close to developing a 55 percent VOC hairspray.

Seaquist

Seaquist manufactures delivery systems for a variety of industries and has attempted to work with both resin and product manufacturers to optimize the hairspray delivery system to accommodate changes in formulations. In the hairspray market, their products are currently used on a few products which claim to be low VOC or no VOC products.

Seaquist indicates of those 30 to 35 formulations provided by approximately 3 resin suppliers and 10 product manufacturers, the primary issues are the atomization and the wetness of the spray. Valve clogging is a secondary issue and can be addressed once the primary issues are adequately resolved. Of the formulations submitted to Seaquist, they believe only one formulation had a high degree of atomization; unfortunately the product's high surfactant level caused the spray to foam (a characteristic which is undesirable in hairsprays).

F. Estimate of 55 Percent Aerosol Hairspray Materials Cost

Based on our discussions with industry representatives, we believe the concerns raised regarding the potential for cost increases primarily involve aerosol hairsprays. To evaluate the expected cost impacts the 55 percent VOC standard may have on aerosol hairsprays, we conducted a materials cost analysis of nine formularies published in recent issues of *Spray Technology and Marketing*. For the purpose of the cost analysis, we assumed products relying on these formularies will meet basic consumer performance needs based on the performance claims cited in *Spray Technology and Marketing*. We conducted a raw materials cost analysis since we expect no significant cost differences in packaging costs. Because these formularies employ various combinations of water, ethanol, hydrocarbon propellants, HFC-152a, dimethyl ether, and resins in varying weight percentages, we believe it is reasonable to assume these formularies are representative of the possible formulation approaches manufacturers are likely to take to meet the 55 percent VOC standard (see Appendix C for formulation details and references).

Using current price quotes for the individual ingredients, we estimated total material costs for each formulary and plotted them against the estimated material costs for representative pre-regulatory anhydrous (*Spray Technology and Marketing*, p. 37, March 1992, Vol. 2, No. 3) and post-regulatory 80 percent VOC compliant aerosol hairsprays (*Spray Technology and Marketing*, p. 36, June 1992, Vol. 2, No. 6). The major materials cost variables were found to be the supplied price of HFC-152a and the resins. Without concrete projections on the expected price of HFC-152a, we used the current price of $1.95 per pound with the expectation that a significant increase in both the supply and market competition for HFC-152a will result in a price reduction for this commodity in the near future. We then chose "best-case" and "worst-case" costs for the resins based on our discussions with industry, resulting in two different price scenarios for each of the nine formularies (i.e., a total of eighteen (9 x 2) cost permutations were calculated and plotted). The best and worst-case costs for resins were assumed to range from about $3.50 to $7.00 per pound, based on quoted prices from several resin suppliers (see Attachment C; Eastman Chemical, Rohm and Haas, and National Starch and Chemical Company) and discussions with industry representatives. The costs for ethanol (SD-40, $0.40/pound), water ($0.002/pound), n-butane (A-17, $0.25/pound), and dimethyl ether (DME, $0.40/pound) are generally known in the industry and are assumed to remain constant for the purposes of this analysis.

The results of the materials cost analysis are shown in Figure 1. The gray shaded area represents the "reference cost range" for the pre-regulatory anhydrous and post-regulatory 80 percent VOC compliant formulas (reference cost range = $0.50 to $0.75 per pound of product; the range is due to the range in resin costs). As Figure 1 shows, at least six of the nine formularies can be formulated with costs that are less than or within the reference cost range. In addition, one formulary with potential use in professional salons (based on a HFC-152a/DME combination) had an estimated materials cost that was only eleven cents ($0.11 per pound) greater than the reference cost range. Thus, seven of the nine published 55 percent VOC compliant formularies can be produced at or slightly greater than the reference cost range of $0.50 to $0.75 per pound.

Fig. 1 Cost Comparison of Nine Reported 55% VOC Formularies

To obtain a copy of this table, please contact Mr. Edward Wong, Associate Air Pollution Specialist at (916) 327-1507**.**

Based on this cost assessment along with our technology assessment, we believe it is likely that manufacturers will be able to produce satisfactorily-performing, aerosol products for both the household retail and professional salon markets within the current estimated materials cost of $0.50 to $0.75 per pound. Therefore, manufacturers should be able to provide products which meet the 55 percent VOC standard and have little, if any, difference in materials costs relative to the reference cost range for pre-regulatory and currently compliant, 80 percent VOC products. Our discussions with industry representatives indicate that manufacturers should not need to expend significant additional capital for any of these approaches, regardless of the type of propellant or other material which are reasonably expected to be used.

VI. METHODS OF COMPLIANCE
(TO BE ADDED)

VII. RECOMMENDATION
(TO BE ADDED)

VIII. ISSUES

A. State Implementation Plan for Ozone - Implications if Hairspray Standard is Amended

Phase I of the consumer products regulation, including the hairspray standards, was adopted by the Board in October 1990. The hairspray category has two standards. One, an 80 percent VOC standard, was effective January 1, 1993; the second, a 55 percent VOC standard, will be effective January 1, 1998. On November 15, 1994, the ARB adopted the State Implementation Plan (SIP) for Ozone. The SIP serves as California's overall long-term plan for the attainment of the federal ambient air quality standards. On August 21, 1995, the U.S. EPA formally approved the consumer products regulations as a SIP revision. This regulation includes both the 1993 and 1998 hairspray standards.

Hairsprays are the largest single emissions category in the consumer product arena, with 46 tons/day VOC emissions estimated for 1990 in the Technical Support Document for the original consumer products rulemaking. However, after compiling and refining the consumer products registration data, it now appears that the emissions from hairspray may be higher than the original estimate. These new data will be reflected in the next comprehensive ARB SIP revision. To put this value in perspective, the next largest category is automotive windshield washer fluid at 24 tons/day. The third largest category in terms of emissions is insecticides at about 9 tons per day. The majority of the remaining categories are smaller emissions sources, with the majority at about 1.5 tons per day or less.

Because the emissions from hairsprays are so significant, the emissions reductions obtained from hairsprays are critical to the success of the consumer products regulation and are a key element of the SIP. Many areas are relying on the emission reductions from hairsprays. For example, San Joaquin Valley and San Diego rely on the reductions from the 55 percent VOC standard to demonstrate attainment for the Federal ozone standard in 1999. Other areas used the reductions to meet the rate-of-progress requirements for 1999 and future years. The 1993 standard for hairsprays was estimated to result in approximately 7.2 tons/day reductions in emissions. With population growth factored in, the second tier reduction is projected to be approximately 14 tons/day in 1999 (see Table 4).

Table 4

Emissions from Hairsprays in 1999 and Reductions Claimed in SIP			
SIP area	**Emissions in 1999 with 55% standard in effect in 1/1/1998**	**Emissions in 1999 if hairspray standard does not go into effect**	**SIP reductions claimed**
South Coast	13.2	19.1	5.9
San Joaquin Valley	3.3	4.8	1.5
Sacramento Region	2.0	2.8	0.8
Ventura	0.7	1.1	0.4
San Diego	2.7	4.0	1.3
Southeast Desert	0.3	0.5	0.2
Statewide	**31.8**	**46.0**	**14.2**

Overall, the hairspray standard achieves approximately a 42 percent reduction in VOC emissions from hairsprays. To put this in perspective with other categories, the insecticides category results in approximately 44 percent reductions from the first tier and 53 percent when the second tier standard goes into effect. Therefore, the reductions required from hairspray are not disproportionate to the emissions required from many of the other consumer products categories.

In fact, the reductions from hairsprays are all the more important when compared with the many district regulations designed to help in District attainment and/or rate-of-progress plans. In general, districts are relying on very small incremental reductions to help them fulfill their plan requirements because the larger emission categories have already been controlled. For example, many new local measures in the Sacramento region project emissions reductions of approximately 0.1 tons/day in 1999, with regulated processes resulting in these kinds of emissions reductions including sources such as pleasure craft refueling and pleasure craft coating. In contrast, the reductions from the second tier hairspray standard are projected to be about 0.8 tons/day in the Sacramento region, as shown in the Table 5. Additionally, a new state measure, California Industrial Equipment standard projects a total of approximately 4 tons/day VOC emission reductions by 2002 in the South Coast. This reduction is in comparison to the approximately 6 tons/day from the second-tier hairspray standard achieved in 1998 in the South Coast region.

Amending or postponing the standard for hairspray, or any other standard in the consumer products regulation, without making up the reductions elsewhere, would constitute a "relaxation" of the SIP. Under the Clean Air Act, this action would be unapprovable by the United States Environmental Protection Agency (U.S. EPA). If ARB approved the relaxation even though it was unapprovable under the Clean Air Act, two things would be likely to happen: 1) U.S. EPA could bring enforcement action against manufacturers who did not meet the current limits in the SIP, even if they met any new relaxed limits that the ARB might adopt; 2) a SIP shortfall would result, and the U.S. EPA could issue a SIP call requiring the ARB to mitigate the loss of emission reductions as a result of the relaxation. Sanctions would eventually be imposed against the state if the ARB did not modify the SIP to make up the emission reductions. Therefore, to address the SIP relaxation issue and avoid the negative repercussions of a SIP relaxation, it would be necessary to replace any "lost" emission reductions. For example, if the 55 percent standard is postponed, the lost emission reductions would have to be made up in the interim period during which the standard was delayed. If the standard is relaxed, the lost reductions must be permanently replaced with alternative reductions. It would be necessary to make up those 1999 reductions with a new state regulation not already defined in the SIP, or, if replacing emission reductions for an interim period, it would be possible to accelerate the implementation date of an ARB SIP commitment. If a SIP revision was submitted to U.S. EPA with another adopted regulation that makes up the shortfall, the U.S. EPA could approve the revision as "emissions neutral."

B. Time to Reformulate

The 55 percent VOC standard effective January 1, 1998 for hairsprays was adopted by the Air Resources Board on October 11, 1990. At that time, the Board found that the standard was both technologically and commercially feasible and necessary to achieve needed emission reductions from the consumer products. The supporting documentation for this regulatory action included a discussion on efforts that were underway by members of industry to develop low VOC hairsprays and reported that, even in 1990, there were many aerosol and pump hairsprays marketed at that time that met the 1998 55 percent VOC standard. It was concluded that, with the additional 7-8 years prior to the 55 percent standard being effective, those manufacturers that did not already have complying products could develop products to meet the 55 percent VOC standard.

Based on the information presented to the ARB staff on October 19, 1995 and in subsequent discussions with manufacturers, it appears there are many companies that need more time for their reformulation efforts. They have stated that the 55 percent standard is achievable, but due to problems with reformulation, additional time is necessary to develop viable products. While the technical literature and patents reflect substantial progress toward developing low VOC hairspray formulas, these manufacturers claim that the formulas would not be marketable by 1998 and additional research and development is necessary to ensure full consumer acceptance of optimized formulas. Because of this, ARB staff has concluded that it is appropriate to explore options that would provide some additional time for reformulation provided: (1) the SIP is kept intact, and (2) those companies that have been successful in developing low VOC products would not be disadvantaged.

Note: To obtain hard copies of the appendices, please contact Mr. Edward Wong, Associate Air Pollution Specialist at (916) 327-1507

APPENDIX A:

OCTOBER 19, 1995 PRESENTATIONS BY CTFA HAIRSPRAY GROUP

APPENDIX B:

SALES BROCHURE AND PRODUCT ADVERTISEMENTS

APPENDIX C:

COST CALCULATIONS