APPENDIX F: 1999 TECHNICAL ASSESSMENT OF AEROSOL ADHESIVES

1999 Technical Assessment of Aerosol Adhesives

In 1996 ARB staff conducted a technology assessment on aerosol adhesives and identified several potential methods for reducing the amount of VOCs in aerosol adhesives. The 1998 Aerosol Adhesives Survey included a section on manufacturers' research and development efforts to update staff's earlier assessment. The survey was structured to gather information on the various methods of reducing VOCs: use of alternative solvents, use of alternative propellants, increasing the solids content, and hardware modifications. This discussion summarizes staff's 1999 technical assessment and the information gathered from the survey as well as information gathered from follow-up discussions and meetings with the industry. The discussion on reformulation efforts is preceded by a brief discussion on present day formulations.

A. Present Formlations

Aerosol adhesives are composed of active ingredients (eg. rubbers, resins, and additives), solvents, and propellants. The solvent and propellant portions of the formulations generally contain VOCs. Typical VOC solvents are aliphatic compounds such as pentane, hexane, cyclohexane, heptane, and aromatic compounds such as toluene and xylene. The survey results indicate that there are also a few alternative compounds presently being used in formulations. Acetone is by far the most popular of the exempt compounds. There are also about 30 products using methylene chloride, perchloroethylene or trichloroethylene. See Appendix E for more details on methylene chloride use. Water and parachlorobenzotrifluoride are also used in some aerosol adhesive formulations. The solvent content of aerosol adhesives range between 18 to 79 percent and average about 39 percent.

Typical VOC propellants are propane, butane, isobutane, and dimethyl ether. The propellants HFC-134a and HFC-152a are non-VOCs which are used in other consumer products. However, neither compound is currently being used in aerosol adhesive formulations. Propellant contents in aerosol adhesives range from 15 to 68 percent and average about 36 percent.

B. Reformulation Options

The following is a discussion of the research and development portion of the 1998 Aerosol Adhesives Survey. The technologies are presented in the following order: solvents, propellants, high solids, and hardware modifications.

Solvents

Water

Some manufacturers have pursued water-based technology. This technology offers advantages of reducing safety concern such as flammability, and lowering the VOC content.

Until recently, there has been one water-base product on the market since 1998. The manufacturer has reported several major problems associated with water-base formulations. The major problems are freeze thaw stability (solidifies in cold weather and does not revert back, even with vigorous agitation), and lengthy drying times. Because of the freeze thaw stability problem, the product must be manufactured, shipped, and stored in above freezing temperatures. In addition, the long drying times slow production for industrial users. Other problems reported by the manufacturer were poor adhesion to non-porous surfaces, wrinkling of paper, poor spray pattern, corrosion of unprimed or unpainted metals, and short shelf life. In addition, other manufacturers have reported problems with excessive foam and clogging of valves and actuators.

The manufacturer of the commercial product has recently announced that the product has been discontinued. The product had been sold primarily to users in non-ventilated work areas. The company has had to discontinue production because of poor performance, manufacture, and storage problems and the unavailability of key raw materials by the suppliers.

Methylene Chloride

Methylene chloride was reported to be a good, fast drying solvent and is compatible with most aerosol adhesive formulations. Methylene chloride is also a non-VOC. However, methylene chloride has been identified by the ARB as a toxic air contaminant. Furthermore, U.S. Occupational Safety and Heath Administration (OSHA) has instituted workplace exposure limits and medical surveillance requirements for workers exposed to levels exceeding the specified exposure limits. The survey results show that a few manufacturers are currently using methylene chloride in their formulations. Of the eight products that meet the future 25 percent VOC standard seven are formulated with methylene chloride and one with water. Discussions with manufacturers indicate that products formulated with methylene chloride are generally older formulations that

are still in demand because of certain desirable characteristics such as faster drying time or low solvent soak in. Several manufacturers have stated that they would not pursue this solvent technology because of its toxicity and that many users have requested non-chlorinated products. Many products even advertise on the label "non-chlorinated." ARB staff is not considering the use of methylene chloride as a reformulation option.

Acetone

Acetone is a fast drying solvent that has been widely used in aerosol adhesives. The ARB approved the exemption of acetone as a VOC due to its low reactivity (potential to form tropospheric ozone) on September 28, 1995.

The previous 1996 technical assessment determined that there were few formulations based on acetone substitution. At that time, several technical issues were reported: substrate attack, insufficient adhesion, misting, and a shortened shelf -life. However, the 1998 survey indicated that acetone is now by far the most widely used method of reducing the VOC content of the formulation. Table F-1 compares the number of products using acetone formulations to other product formulations. Some solvents listed in Table F-1 are combinations of two solvents: acetone/MeCl, water/acetone, water/TCE and MeCl/Perc.

Table F-1: Distribution of Solvent Compositions

Solvent*	Number
Acetone	76
Acetone/MeCl	3
Acetone/TCE	1
Water/Acetone	1
MeCl	26
MeCl/Perc	2
Perc	1
Water	1
All VOC	25

*Methylene chloride and perchloroethylene, trichloroethylene are indicated by the abbreviations MeCl, Perc, and TCE.

Aerosol adhesive manufacturers reported that acetone is a good substitute for VOC solvents because it is readily available, reasonably priced, fast evaporating, and has an acceptable odor. However, formulators have experienced incompatibility with the rubbers/resins at high concentrations of acetone. In general, the maximum content of acetone tolerable in the solvent mixture is about 50 percent. We expect that many manufacturers will be able to further lower the VOC content of their aerosol adhesives by replacing some solvents with acetone. Of the products reported in the 1998 survey, acetone comprises about 20-60 percent of the solvent. However, some specialty products have typical acetone levels ranging from 60-90 percent of the solvent. The properties of acetone are summarized in Table F-2.

Table F-2: Physical Properties of Acetone*

Formula	CH_7COCH_3
Molecular Weight	58.1
Boiling Point, degrees F (C)	133 (56)
Vapor Pressure, mm Hg @ 20^o C	185.5
Evaporation Rate, n-BuOAc=1	5.6
Density, g/cc @ 20^o C	0.792
Kauri-Butanol Value	N/A
Surface Tension in Air: dynes/cm @ 20^o C	22.3
Solubility parameter $(cal/cm^3)^{1/2}$	10
Flash Point, TCC degrees F (C)	- 15 (-26)

*Shell Chemical Company

Some manufacturers have reported that acetone in high concentrations produces characteristics that are unacceptable for some applications. One characteristic associated with acetone is it's tendency to make a wetter bond. This is due to the absorption of atmospheric water in the acetone. As the acetone is rapidly volatilizing, the surrounding air is cooled, causing water to condense. The water is then absorbed in the acetone. This problem is critical in bonding porous materials requiring low soak-in. If the solvent soaks into the substrate, the adhesive is carried with the solvent below the surface, leaving less adhesive on the surface for bonding.

Another characteristic of acetone is its ability to dissolve polystyrene. Polystyrene is manufactured in several forms. Low density polystyrene (beadboard), such as that used in foam cups and packing material, can readily dissolve in acetone. High density polystyrene, known as Styrofoam®, is more resistant to acetone attack. Some manufacturers have formulated their products to minimize acetone attack by using less acetone. Others have modified their formulations by adding some slower evaporating components to protect the surface while the acetone is evaporating or by making the solvent fast evaporating to minimize surface contact time with the acetone. Also, allowing the surfaces to dry to a tack helps to allow acetone to evaporate before bonding. One product has instructions on the can advising users to hold the can a distance of 12 to 15 inches to allow time for the acetone to evaporate.

Methyl Acetate

Methyl acetate is a fast drying solvent and is considered an exempt compound. It has an evaporation rate and solvency similar to acetone, but differs in odor and other properties. The ARB approved the exemption of methyl acetate as a VOC due to its low reactivity in the atmosphere on November 19, 1998. Table F-3 shows the properties of methyl acetate.

Table F-3: Physical Properties of Methyl Acetate*

Formula	$C_3H_6O_2$
Molecular Weight	74.09
Boiling Point, degrees F (C)	132 (56)
Vapor Pressure, mm Hg @ 20^o C	171.3
Evaporation Rate, n-BuAc=1	5.3
Density, g/cc @ 20^o C	0.93
Kauri-Butanol Value	N/A
Surface Tension in Air: dynes/cm @ 20^o C	N/A
Solubility parameter $(cal/cm^3)^{1/2}$	N/A
Flash Point, TCC degrees F (C)	9 (-13)

* Eastman Chemical Company

Currently, methyl acetate is not used in aerosol adhesive formulations. Five manufacturers indicated that they have tested it. However, only two companies reported results in the detailed section of the survey. Two others reported that they plan to test methyl acetate. Manufacturers have reported that in general it behaves similarly to acetone, but it is more expensive (54¢/lb versus 14¢/lb). One manufacturer reported that the solubility is unacceptable and that it dries too slowly.

Parachlorobenzotrifluoride (PCBTF)

PCBTF (also known by the trade name Oxsol 100) is a solvent that is an exempt compound and has the potential to be used in modest amounts in aerosol adhesives. The physical properties of PCBTF are shown in Table F-4. The ARB

TABLE F-4: Physical Properties of PCBTF* (Oxsol 100)**

Formula	$C_7H_4F_3Cl$
Molecular Weight	180.5
Boiling Point, degrees F 8	282 (139)
Vapor Pressure, mm Hg @ 20^o C	5.3
Evaporation Rate, n-BuAc=1	0.9
Density, g/cc @ 20^o C	1.34
Kauri-Butanol Value	64
Surface Tension in Air: dynes/cm @ 20^o C	25
Solubility parameter $(cal/cm^3)^{1/2}$	8.6
Flash Point, TCC degrees F 8	109 (43)

* Occidental Chemical Corporation
** Oxsol 100 is a registered trade name of the Occidental Chemical Corporation

approved the exemption of PCBTF as a VOC due to its low reactivity on September 28, 1995. In addition, PCBTF is not an ozone depleting substance or a federal hazardous air pollutant. PCBTF is used in non-aerosol coatings, inks, adhesives and other resin applications (Occidental Chemical). However, the staff is aware of just one aerosol adhesive product on the market that contains PCBTF.

Four manufacturers have indicated that they have tested PCBTF. Three companies reported results. One company reported that it has an offensive odor, slow dry time, and high price. Another manufacturer reported problems with the spray pattern. A third reported solubility problems.

The odor associated with PCBTF is similar to the odor associated with sanitizing agents and disinfectant sprays. However, masking agents are available that can be used to alter the natural aromatic odor of PCBTF . The drying time of PCBTF is slower than that of toluene, which is already considered to be a slow drying solvent. Therefore, PCBTF, if added, can be added only in limited amounts. In regards to costs, PCBTF costs $1.70/lb. For comparison, toluene is about 12¢/lb. However, it is expected that it would be used in relatively small amounts

due to its slow dry time. In regards to solubility, PCBTF, being similar to toluene, is a good substitute for toluene. Unfortunately, there are only about 30 formulations that include toluene or xylene and the amount added is generally less than 5 percent of the total formulation. One manufacturer said that aromatics are not suitable for aerosol adhesives in large amounts because they are slow drying and because some aromatics are Proposition 65 compounds.

Other Solvents

Staff also inquired about two other solvents: volatile methyl siloxanes (VMS) and t-butyl acetate. VMS fluids are low molecular weight silicone fluids. They are low in toxicity and almost odorless. The evaporation rates are on the same order as butyl acetate. In response to the survey, two companies indicated that they have tested VMS, and four companies responded in the detailed section of the survey. Of the companies that tested VMS, one responded that the evaporation rate is too slow, the solvent has poor solubility, and that it is expensive. The other company reported stability problems. The remaining companies basically had the same comments. However, one company had additional comments: high soak-in, and long term adhesion and durability problems.

Staff inquired about t-butyl acetate after the survey was mailed out. T-butyl acetate is not yet labeled as an exempt compound. However, it will be proposed for exemption by the ARB in the near future. One company responded that t-butyl acetate had poor solubility, was slow drying, and had an unacceptable odor. A second company had not conducted testing but responded based on general knowledge that is was slow drying, had an odor, and thought that, being an oxygenated compound, it would behave like acetone.

Propellants

Hydrofluorocarbon-152a (HFC-152a)

HFC-152a (or Dymel 152a) is a non-VOC propellant that can be used in limited amounts to replace the hydrocarbon propellants currently used in aerosol adhesives. Also, unlike CFC's and HCFC's, HFC-152a is not an ozone-depleting substance. Table F-5, lists the properties of HFC-152a. The vapor pressure of this product is close to that of dimethyl ether, which is a commonly used

propellant in aerosol adhesives, and its low molecular weight means that a relatively small amount of product would produce an acceptable degree of atomization.

TABLE F-5*: Physical Properties of HFC-152a (Dymel 152a)**

Formula	CH_3CHF_2
Molecular Weight	66
Boiling Point, degrees F (C)	-13 (-25)
Vapor Pressure, psig (bar) @ 70^o F (21^o C)	63 (4)
Vapor pressure, psig (bar) @ 130^o F (54^o C)	177 (12)
Density, g/cc @ 70^o F (21^o C)	0.91
Kauri-Butanol Value	11
Flammability Limits in Air, vol. %	3.9 to 16.9
Flash Point, degrees F (C)	< -58 (< -50)

* E.I. du Pont de Nemours and Company (Du Pont)
** Dymel 152a is a registered trade name of E.I. du Pont de Nemours and Company

HFC-152a is not currently used in solvent-based aerosol adhesives. However, the one water-based formulation did use this propellant. HFC-152a is commonly used in other aerosol consumer products, such as hair care products. Seven manufacturers have indicated that they have tested HFC-152a. Six manufacturers have reported their findings. The biggest complaints were the cost and incompatibility with adhesive rubbers and resins. Two manufacturers reported problems with the spray pattern. One manufacturer commented that the hair spray industry has priority for allotments and that this may cause availability problems. One manufacturer reported that, for his products, HFC-152a can be used in small amounts (up to 15%) without sacrificing stability. Another manufacturer reported 4-5 percent substitution. One manufacturer also reported that, if acetone is in the formulation, then the percent acetone may need to be decreased to maintain stability. The manufacturer speculated that some products may achieve VOC levels of 55-60% when used in combination with acetone.

HFC-152a is more expensive than other propellants. HFC-152a costs $1.85 per pound, compared with approximately 22¢ per pound for hydrocarbon propellants. HFC-152a, if used, would be added in limited quantities because of costs and solvency limitations.

Compressed Gas Propellants

Compressed gas propellants such as carbon dioxide and nitrogen have been used successfully in aerosol products for many years, but have not yet been used in aerosol adhesives. Four manufacturers have indicated that they have tested the technology, and seven responded to the survey. The major concern is the lack of solubility of the gas in the mixture. Compressed gases are limited to the small headspace in the can. Because of the small amount of pressurized gas that can fit into the can, the spray pattern is inconsistent throughout the life of the product. Manufacturers also expressed other disadvantages of using compressed gases. Because these gases would comprise such a small percentage of the contents of the can, their presence would not lower the VOC much and they do not contribute much to drying the adhesive during delivery.

In contrast, liquefied hydrocarbon propellants provide a superior spray system. Because these propellants are miscible with the solvent and will vaporize to replenish the headspace as needed, the spray will remain constant throughout the life of the product. Also the vaporization of the propellant helps to break up the adhesive stream.

Other Technologies

This section discusses high solids formulations and hardware modifications.

High-solids Formulations

Manufacturers can reduce the VOC content of their products by increasing the percent of solids (polymers and resins). Nine manufacturers have indicated that they have tested high-solids formulations. Seven have reported their findings. The majority reported minimal reductions in VOC, increased viscosity, and poor spray pattern. Manufacturers reported that increasing the solids content in conjunction with acetone substitution could reduce the VOC content in web sprays. One manufacturer has reported success in combining high solids with acetone and using patented hardware modifications. The company has reduced the VOC content in its formulation by over 10 percentage points and expects further reductions.

A potential advantage of high solids aerosol adhesives, beyond a reduction in VOC content, is that the increased adhesive solids level may allow more coverage. This is because more solids can potentially cover more surface area.

High solids products also have some potential disadvantages. Due to the high cost of polymers and resins, high solids formulations tend to cost more than conventional lower solids formulations. One manufacturer reported that the

solids cost 4 to 5 times more than the solvent. However, the cost per square footage may be less.

Hardware Modifications

Modifications to the hardware can indirectly assist in lowering emissions by accommodating formulations with higher solids, improving transfer efficiency, or reducing the spray rate. Six manufacturers indicated that they have performed testing in this area. The responses indicated that the effects would be minimal. Only one manufacturer stated that hardware modifications would be used in conjunction with other technologies to achieve markedly lower VOC levels.

Achievable VOC Levels

Based on the survey responses and on discussions with manufacturers, we have determined that manufacturers will not be able to meet the 25% VOC standard by January 1, 2002 unless they reformulate with methylene chloride. Originally, the 25% VOC standard was based on reformulating with water as the solvent. Manufacturers have not been able to formulate an acceptable water-based product. Staff has found that there are presently no other exempt compounds or solvents that can be used to lower the VOC content to 25 percent.

The U.S. EPA has received petitions to review many other solvents for consideration as exempt compounds. To qualify for exempt status a compound must meet low reactivity, low ozone depleting, and low toxicity standards. Manufacturers do not see any compound near exemption status that is suitable as a solvent in aerosol adhesives.

However, manufacturers have existing products and can reformulate to meet VOC levels lower than the existing 75% VOC standard. Based on the product survey, some products are at or below 60 percent VOC content. Some manufacturers have already taken the lead to optimize the reformulating options discussed earlier and there are indications that some improvement can be made for some products.

Manufacturers have stated that they can reformulate their products below the current 75% VOC standard using a combination of technologies. These include formulating with non-VOC or exempt compounds, increasing the solids content, and hardware modifications. Manufacturers anticipate that they can employ several of these reformulation methods, either alone or in combination, to achieve lower VOC levels. Specifically, these would include

- Replacing some of the solvents with acetone, methyl acetate, or parachlorobenzotrifluoride;
- Replacing some of the hydrocarbon propellant with hydrofluorocarbon-152a;

- Increasing the proportion of solids.

- Increasing the solvents at the expense of the propellants in order to increase the acetone level; and

- Developing new delivery systems.

In Chapter VI staff proposes the categories and limits shown in Table F-6. Staff believes that these limits are technologically and commercially feasible.

Table F-6: Category Limits

Product	Weight Percent VOC
Mist Sprays	65
Web Sprays	55
Special Purpose	
Mounting	70
Flexible Vinyl	70
Automotive Headliner	65
Expanded Polystyrene Foam	65
High Pressure Laminate	60
Polyolefins	60

Staff expects that the first two categories mist and web, will contain most of the products. Web sprays can achieve a lower VOC level than mist sprays because web sprays have a higher solids content. With a higher solids content, there is less room proportionately for VOC components in the formulation. There are presently no complying products for the web category, but industry believes that based on the ability of web sprays to take on a higher solids content, the 55 percent level can be achieved with further increases in the solids level and increased acetone substitution. Since acetone can generally be substituted up to approximately 50% of the solvent content, the ratio of the propellants/solvents can be modified to allow a higher acetone content. Mist sprays, on the other hand, have a lower solids/solvent ratio to maintain the mist spray pattern. The higher level of solvents results in higher VOC levels. The limit 65 percent reflects this.

The remaining categories all fall under the special purpose category. These products are used for sensitive substrates, demanding applications such as high strength or high heat, or substrates that are difficult to bond. In some cases, these substrates are sensitive to acetone attack. In other cases, these applications may require the use of special rubbers that are difficult to dissolve in acetone. An aerosol adhesive is a complex mixture of components that must remain dispersed or in solution in order to be effectively applied. Acetone

substitution, which is the major method of lowering VOC, is not as effective for products formulated primarily for special purpose applications.

The applications in the 70 percent category are composed of flexible vinyl and mounting adhesives. There is presently only one product that staff is aware of that is designed primarily for vinyls. This is a neoprene adhesive, which is very difficult to solubilize. There are other products that can be used on unsupported vinyl (vinyl with cloth backing). Nevertheless, manufacturers claim that plasticizers can still migrate from the vinyl to the adhesive. Adhesives that are resistant to plasticizers have a higher molecular weight. These rubbers are less soluble in solvents and will require a higher solvent/rubber ratio, thus a higher VOC. There are two mounting adhesives that are widely used for professional mounting by framing shops. The adhesives are marketed for permanently bonding posters and prints to a backing without causing discoloration. These products cannot be reformulated to levels below 70 percent VOC because of potential harm to the substrate. Therefore, to ensure the availability of aerosol adhesives for mounting, the limit was set at 70 percent VOC.

The applications in the 65 percent category are composed of headliners and polystyrene foam. Headliners require a high strength, high temperature contact adhesive. These products are made from styrene-butadiene rubbers, which are difficult to solubilize. Manufacturers need flexibility in solvent selection. The other application, polystyrene foam, is sensitive to substrate attack by acetone. Although the severity of acetone attack can be minimized by proper application, the homeowner does not always read the label carefully. Misapplication can severely damage polystyrene. Also, there are times when a heavier film needs to be applied for added strength. If too much adhesive is applied over the same area too quickly, the acetone may sit on the surface long enough to attack the foam. Manufacturers are concerned about product liability and therefore need to restrict acetone use in the formulation to allow the product to be more forgiving.

The applications in the 60 percent category are composed of high-pressure laminate bonding and polyethylene sheeting. High pressure laminate comes in thin, tightly rolled sheets. High strength, quick bonding spray adhesives are generally used for bonding high-pressure laminate because of the tendency of the sheet to curl while it is bonding to the wooden surface. Web spray contact adhesives are usually marketed for this application. There are currently a couple of products available at around 60 percent VOC. Manufacturers are uncertain whether they can formulate a 55 percent VOC product by 2002. Therefore, the limit is based on a level of 60 percent to ensure that complying products will be available by 2002.

Polyolefins have very low energy, and, therefore, have little to no attraction for anything to which they come in contact with. Adhesives used for polyolefins serve an important function in containing asbestos dust during demolition. There are currently a few products available at 60 percent VOC. Manufacturers are

uncertain whether they can formulate a 55 percent product by 2002. Therefore, the limit is based on a level of 60 percent to ensure that complying products will be available by 2002.