Using VOC-Exempt Solvents To Formulate Compliant Coatings

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The recent decision by the United States Environmental Protection Agency (EPA) to exempt acetone from regulation as a volatile organic compound (VOC) has focused attention on the potential for using VOC-exempt solvents to reduce VOC emissions and comply with increasingly stringent regulatory requirements. This article briefly reviews the regulatory status of VOC-exempt solvents and discusses the role that they can play in helping formulators and solvent users to meet regulatory requirements under the federal Clean Air Act and similar state laws. It then uses acetone as a case study to show how a VOC-exempt solvent can allow a coating operation to meet stringent regulatory standards, while at the same time continuing to use proven solvent systems and existing application equipment.

It is beyond the scope of this article to compare the costs of different options for meeting regulatory requirements. In many cases, however, reformulation using a VOC-exempt solvent may be less costly than using water-based systems or other alternative technologies.

Background

Virtually all ink and coating operations--regardless of whether they use solvent-based or water-based systems or alternative technologies--are faced with a variety of regulatory requirements. Water-based coatings, for example, are likely to trigger regulatory requirements regarding the handling and disposal of solid waste and the control of water pollution. For users of solvent-based inks and coatings, the greatest regulatory challenge may be the need to comply with regulations on VOC emissions.

Virtually all organic solvents used in inks and coatings are VOCs. Emissions of VOCs, in and of themselves, do not necessarily give rise to health or environmental concerns. In many areas, however, they react photochemically in the atmosphere with oxides of nitrogen (NOx) to form ground-level ozone--the primary component of “smog.” For that reason, they are regulated as “ozone precursors” under the Clean Air Act.

Although solvent emissions represent a relatively minor portion of total VOC emissions, industry and regulators have recognized the need to focus on all emissions that may contribute to ozone formation. Therefore, VOCs from all sources--including solvent users--will be subject to increasingly stringent regulation over the next few years.

For many years, scientists have recognized that individual solvents and other compounds are not equal in their potential to form ozone. The potential contribution that each VOC makes to ozone formation depends on its photochemical reactivity: the higher the reactivity, the greater the potential contribution to ozone formation. Over the last fifteen years, EPA has developed a list of compounds that have very low or “negligible” reactivity. The Agency has determined that these compounds “do not contribute appreciably to ozone formation,” and has therefore given them VOC-exempt status by excluding them from the regulatory definition of VOC.

As a result, VOC-exempt solvents need not be counted as VOCs for purposes of regulations that affect coating operations. Where a regulation, for example, sets a limit on the VOC content of a particular coating, any VOC-exempt solvent in the coating will not be counted against that limit. Thus, the use of a VOC-exempt solvent in a solvent blend can give a formulator flexibility to use other proven solvents and still meet stringent regulatory standards.

Technical Considerations

In most applications, a VOC-exempt solvent cannot simply be used as a one-for-one replacement for a VOC solvent. Rather, a formulator must balance a number of performance factors in order to develop an acceptable solvent blend for a particular application. Some of these factors are relevant primarily for specific applications. For example, lacquers require careful attention to blush resistance, and electrical conductivity is a key factor for electrocoating and electrostatic spray applications. Most factors, however, are relevant for a wide range of coatings.

A formulator must generally consider the following criteria (in addition to cost) when selecting solvents for a coating formulation: evaporation rate, resin solubility, solvent activity, solvent balance, flash point, and weight to volume ratio.

Evaporation Rate: The first factor to be considered is the evaporation rate of the solvents in the coating, which in turn can affect other important criteria. In particular, evaporation rate can affect drying time and solvent balance and must be suitable for the application method. Spray-applied coatings are formulated with fast evaporating solvent blends for fast drying and minimal sags and runs, while brush applied coatings use slower evaporating solvents for longer open time and smooth flow and leveling.

Resin Solubility: A fundamental solvent requirement is sufficient solubility to dissolve the resin and form a resin solution. In most applications, blends are used rather than single solvents. Each component in a blend has a purpose. The blend must include enough strong, active solvents to dissolve the resin, but usually includes less expensive hydrocarbon diluents as well. The most economical solvent blends generally contain the maximum amount of low-cost diluents that the resin can tolerate and the minimum amount of active solvents necessary to dissolve the resin.

Solvent Activity: Some active solvents are stronger or more efficient than others. Stronger active solvents have higher solvent activity and reduce resin solution viscosity more efficiently. This means that less solvent is required for viscosity reduction and application viscosity is achieved at lower solvent content. Higher solvent activity also confers an economic benefit, as more diluent can be used in the solvent blend formulation.

Solvent Balance: Because each solvent has a different evaporation rate, the solvent composition of a blend changes as evaporation proceeds. It is important to manage the changing composition to maintain solvency and avoid resin precipitation. As noted above, solvent blends usually contain inexpensive hydrocarbon dilutents in addition to active solvents. This may decrease solvency, and if solvency drops too far, the resin will precipitate in the partially formed film--a condition known as “resin blush.” As a rule of thumb, the slowest evaporating solvent should be an active solvent for the resin and not a diluent.

Flash Point: The flash point of a solvent is a critical formulation factor because of its relationship to user safety and shipping and handling requirements. The lower the flash point of a solvent, the greater the concern about flammability. Thus, a formulator must carefully manage the flash point of the overall solvent blend to address concerns about user safety and transportation.

Weight to Volume Ratio: The weight to volume ratio (density) of a solvent has both a regulatory and an economic impact. Permissible VOC emission levels are usually written in terms of grams of VOC per liter of product, or pounds of VOC per pound of solids. The lower the solvent density, the more volume may be included in the formulation for a given weight. Because formulators generally purchase solvents by weight, not by volume, lower density solvents may also confer economic benefit, since less weight is needed to fill a given volume.

Although these are the major factors to consider, other technical issues may arise with individual solvents and applications. Formulators should consult with their solvent supplier before reformulating with any VOC-exempt solvent.

A Case Study

In June 1995, EPA issued a rule exempting acetone from regulation as a VOC. The rule was based on recent studies showing that acetone has only negligible photochemical reactivity and therefore does not contribute appreciably to the formation of ozone.

As a strong, active, VOC-exempt solvent, acetone is attractive to formulators that must meet increasing regulatory pressures to reduce the VOC content of solvent systems, while maintaining performance. Because of the current interest in acetone, this article will use acetone as a case study to show how a VOC-exempt solvent can be used to develop effective solvent blends that meet regulatory requirements for VOCs. Formulators and solvent users should also keep in mind that there are a small number of other solvents that currently have VOC-exempt status, and that others may be given such status in the future as further information about their photochemical reactivity becomes available. The list of all compounds with VOC-exempt status is found at 40 C.F.R. § 51.100(s).

Because of the VOC-exempt status of acetone, some formulators and solvent users may want to increase the acetone content of a formulation to the maximum extent possible. There are, however, several important factors that limit the amount of acetone that may be used in a particular formulation. Because of its particular properties, acetone is especially well suited for use in some applications and generally cannot be used in others.

Evaporation Rate

As noted above, because most coatings and inks rely on solvent evaporation to control the flow and leveling of the system and to prevent sags and runs, the evaporation rate is typically the starting point for any formulation. Selecting the right solvents to blend with acetone depends primarily on the desired application evaporation rate.

Acetone is a fast evaporating solvent with a relative evaporation rate of 5.7 (n-butyl acetate = 1.0). For this reason, it must generally be blended with slower evaporating solvents to achieve the desired application evaporation rate. Although it is possible to blend an extremely slow evaporating solvent with a fast evaporating solvent such as acetone to achieve any evaporation rate in between those of the two solvents, such an approach is very sensitive to temperature changes and should generally be avoided.

Table 1 shows a number of options for blending acetone with other solvents to achieve a range of evaporation rates from 0.5 to 3.0.

The table is intended to be illustrative, as it shows only binary blends -- i.e., blends that contain only two solvents. In practice, a formulator would generally want to use several solvents in order to balance the key performance factors discussed above. Many solvent producers and their distributors offer technical assistance for formulators seeking to use acetone (or any other solvent) in complex formulations designed to achieve specific goals.

For purposes of Table 1, a number of commonly used solvents have been divided into groups based on their evaporation rates. The midpoint of the range of evaporation rates of the solvents within each group was then used to calculate the blends shown on the table. A computer program was used to project the evaporation profile of each blend, including the solvent composition at any point during the drying time.

Table 1. Blends of Solvents with Acetone to Achieve Selected Evaporation Rates
(Ratios of Acetone/Group Solvents Shown by Percent Weight)

Desired Evaporation Rates (n-Butyl Acetate = 1.0)		3.0	2.0	1.0	0.5
Solvent Blend	Evaporation Rate (n-Butyl Acetate = 1.0)				
Acetone	5.7	35%	--	--	--
Group I	1.9 - 2.3	65%	--	--	--
Acetone	5.7	65%	35%	--	--
Group II	1.4 - 1.7	35%	65%	--	--
Acetone	5.7	73%	55%	--	--
Group III	0.9 - 1.1	27%	45%	--	--
Acetone	5.7	84%	77%	60%	20%
Group IV	0.4 - 0.7	16%	23%	40%	80%
Acetone	5.7	86%	85%	80%	68%
Group V	0.12 - 0.3	14%	15%	20%	32%
Acetone	5.7	87%	86%	83%	75%
Group VI	0.04 - 0.08	13%	14%	17%	25%
Acetone	5.7	88%	87%	86%	--
Group VII	0.02 - 0.04	12%	13%	14%	--

Notes to Table 1

1. Table 1 is designed for illustrative purposes only Evaporation rate is only one factor, and the blends shown above should not be used without analysis of all relevant factors.
2. To avoid resin precipitation, the slowest evaporating solvent (the "tail solvent") in a formulation must be an active solvent for the resin system. For this reason, a number of the Illustrative blends shown on Table 1 could not be used in many common resin systems.
3. Blending acetone with solvents from Groups VI and VII will often raise concerns about excessive evaporative cooling and other temperature effects, and will only be appropriate under limited circumstances.
4. Solvent ratios shown above are approximate and will vary with changes in humidity, air flow, and temperature.
5. For all solvent blends, the flash point of the blend must be taken into account to ensure safe use and handling. This is a particular concern for blends with high concentrations of acetone.

Group I	Evaporation Rate	Group V	Evaporation Rate
Methyl Propyl Ketone (MPK)	2.3	VM&P Naphtha ASTM D 3735 Type II	0.3
n-Propyl Acetate	2.3	Cyclohexanone	0.3
Toluene	1.9	Propylene Glycol Tertiary Butyl Ether (PTB)	0.3
		Methyl Isobutyl Carbinol (MIBC)	0.3
		Amyl Alcohol	0.3
		Aromatic 100	0.3
		Propylene Glycol Propyl Ether (PNP)	0.2
		Diisobutyl Ketone (DIBK)	0.2
		Dimethylformamide (DMF)	0.2
		n-Pentyl Propionate	0.18
		Hexyl Acetate Esters	0.17
		Ethyl 3-Ethoxypropionate (EEP)	0.12
		Diacetone Alcohol	0.12
Group II		Group VI	
Ethyl Alcohol	1.7	Propylene Glycol Butyl Ether (PNB)	0.08
Isopropyl Alcohol	1.7	Heptyl Acetate Esters	0.08
VM&P Naphtha ASTM D 3735 Type I	1.6	Aromatic 150	0.06
Methyl Isobutyl Ketone (MIBK)	1.6	Ethylene Glycol Butyl Ether (EB)	0.06
Isobutyl Acetate	1.4	Cyclohexanol	0.05
		140 Flash Solvent	0.05
		Mineral Spirits ASTM D 23 Type II	0.05
		n-Methyl Pyrrolidone (NMP)	0.04
Group III		Group VII	
2-Nitropropane	1.1	Octyl Acetate Esters	0.03
n-Butyl Acetate	1.0	Ethylene Glycol Butyl Ether Acetate (EB Acetate)	0.03
n-Propyl Acetate	1.0	2-Ethylhexyl Acetate	0.03
Secondary Butyl Alcohol	0.9	Dipropylene Glycol Methyl Ether (DMP)	0.02
		C-11 Ketone	0.02
		Isophorone	0.02
		Ethylene Glycol Diacetate (EGDA)	0.02
		Diethylene Glycol Methyl Ether (DM)	0.02
		Diethylene Glycol Ethyl Ether (DE)	0.02
Group IV			
Propylene Glycol Methyl Ether (PM)	0.7		
Xylene	0.7		
Isobutyl Alcohol	0.6		
Methyl Isoamyl Ketone (MIAK)	0.5		
Methyl Amyl Acetate	0.5		
n-Butyl Alcohol	0.5		
PM Acetate (PMA)	0.4		
Amyl Acetate	0.4		
Methyl n-Amyl Ketone (MAK)	0.4		
Isobutyl Isobutyrate (IBIB)	0.4		
n-Butyl Propionate	0.4		

Table 1 includes not only individual oxygenated solvents, but also hydrocarbon solvent blends that are commonly used in a variety of inks and coatings. Hydrocarbon solvents are complex mixtures of different compounds, usually characterized by distillation profile and solvency and supplied on a specification basis. This means that there can be numerous blends of a given type of hydrocarbon solvent, each with a different evaporation rate and solvency. For example, one major producer of hydrocarbon solvents markets over twenty different mineral spirits with relative evaporation rates from 0.05 to 0.27. Formulators and end users should discuss their specific needs with their solvent or coatings supplier.

Limitations on Formulating with Acetone

As noted above, the opportunity to use acetone in place of other solvents will be limited to some extent by its fast evaporation rate. There are also other important limitations on the use of acetone. Improper formulation can result in flash points that are too low and drying times that are too fast. It can also create excessive evaporative cooling following application, and potential solvent balance problems. Using too much acetone in a solvent blend can also impair application spray properties and film quality.

Flash Point Effects: Acetone has a flash point of about 0° F. This is much lower than other commonly used, fast evaporating solvents such as methyl ethyl ketone (MEK) and ethyl acetate, which are above 20° F. Therefore, solvent blends that contain significant amounts of acetone will have lower flash points than similar blends formulated with MEK and ethyl acetate. For example, a blend with the composition 30/20/20/15/10/5 toluene/xylene/MEK/MIBK/IPA/EEP has a calculated flash point of 37° F. If the MEK in this blend is replaced with acetone, the calculated flash point of the blend drops to 23° F. This obviously has implications for worker safety as well as shipping and handling.

Solvent Balance Effects: As noted above, a suitable solvent blend not only dissolves the resin initially, but also maintains the resin in solution throughout the entire film formulation period. Most hydrocarbon diluents evaporate more slowly than acetone, and will tend to increase in concentration as evaporation proceeds, thus decreasing the solvency of the blend. If solvency drops too far, the resin will precipitate in the partially formed film and cause resin blush. Since acetone evaporates rapidly, slower evaporating active solvents must also be present to maintain solvency.

Temperature/Humidity Effects: Excessive evaporative cooling can occur if the acetone concentration in the solvent blend is too high. In a warm, humid atmosphere, water will condense on the partially formed film, impairing film integrity and resulting in an unacceptable film whitening known as "humidity blush." To a certain degree, slower evaporating solvents in the blend can mitigate this effect, but during the summertime in humid climates, it may still be necessary to reduce acetone content or even eliminate it from the formulation.

Sprayout Effects: The solvents in a coating system begin to evaporate as soon as the coating is atomized into small particles at the spray gun tip. If the solvent evaporates too fast, the coating thickens excessively and a condition known as "cobwebbing" can occur. Too much acetone can worsen this effect, and the amount of acetone must be adjusted according to spray conditions. In some cases, the sprayed coating will be almost dry when it impacts the substrate, producing weak, dull films. Balancing acetone content with slower active solvents is very important to achieve smooth, glossy films.

Suitable Applications For Acetone

Acetone can be incorporated into a number of applications -- particularly in applications that can benefit from its fast evaporation and strong solvency. Applications that are especially suitable for acetone include spray applied furniture coatings, fast dry industrial coatings, and automotive refinish.

Spray applied furniture coatings, for example, consist primarily of nitrocellulose and acrylic lacquers. Because lacquer films are formed by the evaporation of the volatile solvent system, the selection of components with proper evaporation characteristics is a critical factor in formulating such coatings. Spray applied coatings traditionally contain a balance of fast, medium, and slow evaporating solvents--providing an excellent opportunity for the incorporation of acetone.

As noted above, the final film properties of a coating can be affected by improper balance of evaporation characteristics. If a lacquer system dries too quickly, it leads to moisture blush, or in the case of spray application, to dusting (dry spray) or an uneven surface pattern commonly referred to as “orange peel.” Both moisture blush and flow-out can be improved by including slower evaporating solvents with higher blush resistance, adjusting the fast evaporating solvents (including acetone) to an optimum level, or adding retarder (very slow evaporating) solvents to the system. Note, however, that large amounts of slow evaporating solvents may slow production speeds by unduly increasing drying times and impairing hardness development and can also cause sagging in spray applications.

Acetone can also be used in other types of coating applications, including fast dry industrial and automotive refinish coatings. The criteria for incorporating acetone in these systems are the same as those for lacquers. In all cases, however, the balance of solvents is entirely system dependent. For any coating, the formulator is well advised to consider both compliance with regulatory requirements and optimization of the formulation itself. Solvent suppliers can provide specific examples of a variety of formulations that use acetone to achieve these goals.

Applications Where Acetone Is Not Suitable

The same characteristics that make acetone desirable in many applications limit its usefulness in others. In particular, acetone is generally not well suited for use in water-based coatings, marine coatings, and roller and coil coatings.

Water-based systems require solvents that will couple with the resin better than water. In this case, the solvent evaporates more slowly than the water to create the desired film finish. The need for a slow evaporation rate effectively precludes the use of acetone as the main solvent in any water-based solution or emulsifying system that exists today.

For marine coatings, the worker environment is the most critical factor. The solvent blends used in these applications generally must have high flash points--generally 100° F and higher--and low volatility to avoid high vapor concentrations in the air. The precise requirements are highly dependent on the specific conditions of use, including temperature, humidity, and ventilation. However, with a flash point at 0° F, acetone generally cannot be used in these applications.

In addition, acetone generally is not suitable for coil and roll coating of metals, which are very sensitive to fast evaporation rate. In either air drying or baking applications, surface imperfections often result from rapid drying. In baking systems the rapid evaporation causes skinning and subsequent blistering or detachment of the coating as the trapped or retained solvent attempts to escape.

Measuring Reduction in VOC Content

Regulations that limit the VOC content of coatings typically require that VOC content be measured in one of two ways: (1) in pounds of VOC per gallon of solution minus exempt solvents (including water and acetone); or (2) in pounds of VOC per pound of solids, as applied. The trend in recent regulations is to favor the later method, which is generally considered a better approach because it measures the expected emissions for a given amount of surface area coated to a given film thickness.

Either method will show a reduction in the VOC content of a coating when a VOC-exempt solvent is used in place of other solvents. The reduction is much more dramatic, however, when measured by the “per pounds of solids” method. This disparity results from the requirement that exempt solvents such as acetone be subtracted from both the numerator and the denominator under the “pounds per gallon” method, while they are only subtracted from the numerator under the “per pounds of solids” method.

For example, the VOC content of a typical 15 percent solids lacquer formulation that contains no VOC-exempt solvent would be calculated as follows:

<u>Pounds VOC Per Pounds of Solid</u>

VOC = 85 lbs solvent/15 lbs solids = 5.7 lbs/lb solids

<u>Pounds VOC Per Gallon of Coating</u>

VOC = 85 lbs solvent/13.3 gal = 6.39 lbs/gal.

Such a coating may be reformulated to contain as much as 40 percent acetone by weight, as long as the user takes the lower flash point into account to ensure safe use and handling. Because acetone is a very active solvent, the reformulated coating would actually have a higher solids content than the typical lacquer blend described above and still reduce the resin to the same viscosity.

Because of the higher solids content, it would contain less overall solvent--

approximately 81 pounds versus 85 in the original coating. Acetone would account for approximately 32 of the 81 pounds of total solvent. Because acetone does not count as a VOC, the numerator for both equations is 81 - 32 or 49 pounds of solvent. Under the pounds per gallon method, the acetone (32 pounds = approximately 4.9 gallons) also must be subtracted from the denominator. Thus, the VOC content of the reformulated coating would be calculated as follows:

Pounds VOC Per Pounds of Solid

VOC = 49 lbs solvent/19.2 lbs solids = 2.55 lbs/lb solids

Pounds VOC Per Gallon of Coating

VOC = 49 lbs solvent/13.2 gal - 4.9 gal acetone = 5.9 lbs/gal.

While both methods show a reduction in the VOC content compared to the original coating, the reduction is obviously much greater using the per pounds of solids method (55 percent versus 8 percent). Note that the use of 40 percent acetone in the reformulation actually decreases the VOC content by about 55 percent (based on the per pounds of solids method). This results from the fact that acetone is a strong, active solvent that enables the replacement blend to have a higher solids content than the original blend.

As noted above, measuring the VOC content of a coating per pound of solids is a better indicator of the true environmental impact of a coating and is generally favored in recent regulations. Many regulations, however, continue to require VOC content to be measured in pounds of VOC per gallon of solvent.

Conclusion

Formulators and users of solvent-based inks and coatings are currently evaluating their options for complying with regulations designed to reduce VOC emissions. The feasibility of any individual option will depend on a variety of factors, including the specific application involved and the applicable refulatory requirements.

In some cases, a user may be able to switch to a water-based system or other non-solvent technology. These technologies are likely to trigger other regulatory requirements, however, and are not practical for many applications. Companies that want to preserve the benefits of their existing solvent systems often think that their only option is to install control technology.

In many cases, reformulating with a VOC-exempt solvent such as acetone may be less costly than installing control technology or using water-based systems or other alternative technologies. Where feasible, such an approach will allow solvent users to reduce VOC emissions while continuing to use existing application equipment and proven solvent systems.

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