# An Overview of Solvents Used in Cleaning Applications

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*A Practical, Dual-Track Discussion of*

**How to Manage**
**SOLVENTS**
**in the Workplace**

Track I: Hazardous Solvents // Track II: Cleaning Solvents

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cleaning processes. In this paper, we will use a more limited definition of solvent and limit the detailed discussion to several classes of organic solvents. It is worth noting though, that even in a limited scope, this paper will cover hundreds or thousands of individual chemical compounds and cleaning agents. This work should be used as a guide to help understand some of the nomenclature found in industry, and to begin narrowing the range of choices to a manageable number.

Some of the broadly used solvent processes which we won't consider in this paper, but are covered in detail by others at this conference, are the variety of water-based cleaning agents. Yes, water is a solvent, and an excellent one at that. Sometimes referred to as the "universal solvent," it always has been, and always will be the most broadly used cleaning solvent on earth. However, increased regulatory scrutiny makes the use of water-based processes impractical in some industrial settings. Extremes of pH can lead to undesirable metal dissolution and therefore expensive water disposal/waste treatment. Neutral pH cleaners or deionized water are also excellent solvents for highly ionic materials but they are not necessarily the best choice for the petroleum-based soils so common in the metalworking industry. Finally, some parts and their associated manufacturing processes are simply incompatible with water.

The second class of solvents which will be discussed in detail by others are halogenated solvents. These are organic solvents in that they contain carbon, but they are unique in that they also contain halogens (fluorine, chlorine or bromine) which give them an interesting range of chemical and physical properties. These properties make them excellent choices as cleaning agents, but with some undesirable effects. The by-products of the chemical breakdown of halogenated materials are generally toxic and/or corrosive. One effect of this was that the most stable formulations (CFC-113 and methyl chloroform) were the ones that became the most popular cleaning agents, until it was discovered that they depleted stratospheric ozone. Less stable materials, on the other hand, break down more readily, resulting in ground-level smog formation, human toxicity concerns and corrosive effects on some parts and cleaning equipment. The excellent cleaning characteristics and rapid evaporation of chlorinated solvents guarantee that they will remain a smaller but important part of the cleaning industry.

A new generation of fluorinated materials is now becoming commercially important. HCFCs, HFCs, HFEs and others have interesting and unique chemical and physical properties, but because they tend to be very expensive and are relatively poor solvents, these products will remain niche products.

This brings us to the classes of solvents which are the subject of this paper, hydrocarbon solvents. Before beginning an analysis of the classes of hydrocarbon solvents, let's first examine the factors which affect the choice of solvent process. First, does the solvent dissolve the dirt without dissolving the parts? While this is the most important question, in most industrial applications, the answer is "yes" for virtually all hydrocarbon solvents.

The second question is whether the process can be operated in a way that meets all applicable regulations including workplace exposure guidelines, safety regulations and air emission limits. Unlike the first one, this is a difficult and complex question. Regulatory issues are often affected by layers of federal, state and local laws with which the user must comply.

Finally, you will need to consider whether the process can be implemented effectively and efficiently in your plant. Remember, virtually any process can be made to work and the choice which is the most effective will depend on a series of trade-offs. For example, faster drying solvents are normally more flammable than slower drying solvents. So, the trade-off will be a fast drying solvent with all of the attendant safety and human exposure risks versus a slower drying solvent that may require a more expensive and time consuming drying process.

## Hydrocarbon Solvents

The first class of solvents we will discuss are hydrocarbon solvents. While all of the compounds we discuss from this point on are, strictly speaking, hydrocarbons, for now we will use a narrower definition—those chemical compounds containing ***only*** hydrogen and carbon (for those interested in chemical structures, Appendix 1 contains examples of compounds from chemical families discussed below). Pure hydrocarbons are often defined in three terms:

by their molecular weight, their degree of saturation, and their molecular configuration.

As the molecular weight of a hydrocarbon goes up, so does its flash point, while its vapor pressure or drying rate come down. The solubility properties of hydrocarbons, over the range of molecular weights suitable for use as cleaning agents, changes very little. The degree of saturation depends on whether or not the carbon-carbon bonds are chemically single bonds or double bonds. If all are single bonds, the molecule is described as "saturated." Saturated molecules tend to have lower toxicity and lower odor than unsaturated, but have poorer solubility for most soils. As the degree of unsaturation goes up, stability is reduced, odor increases, and toxicity increases, but solubility characteristics improve.

Finally, structure refers to the way in which the carbon molecules are connected. "Normal" means that all of the carbons are connected end-to-end. "Branched" is self explanatory with branches of carbon atoms off the main carbon chain. And finally, cyclic molecules are those where at least some of the carbon atoms are connected in a ring. Once again, cyclic compounds tend to have better solvency but slightly worse toxicity and sharper odors than their normal and branched analogs.

Several commercial grade hydrocarbon solvents are available under generic names such as white spirits, mineral spirits or stoddard solvent. These products are mixtures of normal, branched and cyclic hydrocarbons and include saturated as well as unsaturated products. These solvents are generally identified by their flash point, which gives the user some information as to the relative volatility of the product. They are products of the petroleum refining process and generally include a wider variety of individual chemical species than the more refined products discussed in the following paragraph. As a group they have slightly better solubility characteristics than purer materials but may contain various levels of impurities such as sulfur or small amounts of aromatics. These products have wide utility in non-critical, large-volume degreasing operations but are not found in difficult or precision cleaning applications.

There are several commercial grades of pure hydrocarbons available. They range in price based on their purity, and are often water-white (clear and colorless) materials. Pure hydrocarbon solvents are enjoying a resurgence in the industry because the higher quality products have relatively low orders of toxicity, little or no odor, and are relatively inexpensive. By themselves they typically have very limited solubility for soils, but as we will discuss later, they are used widely in formulated solvent blends.

## Terpene Hydrocarbons

Terpene hydrocarbons are a unique class of solvents which are derived from "natural sources" such as citrus fruit and pine trees. These compounds are unsaturated, cyclic materials which have excellent solubility characteristics. The fact that they are unsaturated can lead to a degree of oxidative instability and they tend to have low flash points, primarily in the Class II combustible range, 100°F to 140°F. In the mid-1980's, Petroferm began investigating the use of a particular terpene, *d*-limonene, as a substitute for CFC-113 for cleaning rosin from printed circuit boards. This was a particularly difficult cleaning application and led to commercialization of the first CFC alternative cleaning agent.

Terpenes have been used widely in other applications since that time and their use in critical cleaning applications has led to the development of proprietary antioxidant technology which can dramatically improve the stability of the terpene molecules. In summary, terpenes are excellent cleaning agents with a wide variety of solubilities. They do, however, attack some plastics and elastomers, so cleaning equipment gaskets and seals must be selected carefully and the application of terpenes for cleaning plastic parts must be very carefully considered.

Terpene hydrocarbons are also unique in that they have very characteristic citrus or pine odors. While this fact is seen by many as undesirable, the olfactory limits (the concentration which most people can smell) of these materials are well below established exposure limits. If the odor in the workplace is a source of irritation to employees, ventilation should be improved, or work practices modified.

## Aromatic Hydrocarbons

Aromatic compounds are derivatives of a common organic chemical called benzene. Benzene is a six carbon molecule with all of the carbons arranged in a ring. Of the six bonds in this ring, three are single bonds and three are double bonds (this is a gross over-simplification from a chemical standpoint, but sufficient for this work). Benzene has excellent solvent properties but is a known human carcinogen and has no place in the cleaning industry. Several benzene derivatives such as toluene, xylene and ethyl benzene have similar solubility characteristics. These compounds, however, are flammable liquids (flash point less than 100°F) and though they are not classified as known human carcinogens they are relatively toxic when compared to other classes of compounds discussed here.

The unique solubility characteristics or aromatic solvents make them good technical choices in some cleaning applications. However, users must be aware the fact that these compounds have serious toxicity concerns associated with them and can be dangerously flammable.

## Oxygenated Hydrocarbon Solvents

The next broad category of hydrocarbon solvents which we will consider are those hydrocarbons which contain one or more oxygen atoms. These are classified into several types of materials. The presence of oxygen in the molecule tends to make the materials better cleaning agents but they also can tend to have slightly worse toxicity and more dangerous flammability characteristics than the pure hydrocarbons.

## Ethers and Ketones

Ethers, such as methyl tertiary butyl ether (MTBE), typically are very good solvents but they are extremely flammable materials and some have significant toxicity concerns. For these reasons, their use as cleaning agents is somewhat limited and other alternatives should be considered unless there is an overriding reason to use the ether.

An important subset of the ether family are glycol ethers. Traditionally used as components of coating formulations, glycol ethers are now used widely as cleaning agents or components of formulated cleaning agents. Ethylene glycol ethers have recently come under intense regulatory pressure due to their toxicological properties. Propylene glycol ethers, on the other hand, are not nearly as toxic and available in a wide range of pressures and flash points. Their stability and excellent solubility for polar soils make them a popular choice for many formulated cleaning agents. Users of cleaning agents which contain glycol ethers should demand detailed toxicity and regulatory guidance from their suppliers to ensure that applicable human exposure limits are followed and emission limits are met.

Like ethers, ketones, such as acetone or methylethylketone (MEK), are good polar solvents and used widely in many chemical process industries. Once again, they are extremely flammable solvents which must be handled carefully. Equivalent cleaning performance can generally be achieved with higher flash point products.

## Alcohols

The next set of cleaning materials which we will consider are those based on alcohol. Alcohols tend not to be as toxic as other oxygen-containing hydrocarbons but they can be equally as flammable. They are poorer solvents than other oxygen-containing materials but they do have somewhat less odor.

Alcohols are not broadly applicable as cleaning agents because of their limited solubility, though recently there has been a great deal of interest in processes which use alcohols as rinsing agents for other, more aggressive organic cleaning agents. Alcohols are normally miscible (soluble in all proportions) with the cleaning agents, which makes their rinsing effectiveness excellent. They are generally available in very high purity at modest cost so they can be used economically in most applications.

## Esters

The final category of oxygenated solvents which we will consider are esters. Esters have superior solubility characteristics. They are likely the most polar class of solvents available on the market today and indeed are used in difficult cleaning applications, like paint stripping. However, the polarity or the power of these cleaning agents can be a negative in that they tend to be very aggressive toward plastics and elastomers. Once again, gasket and elastomeric materials for cleaning systems must be carefully chosen, and the use of these cleaning agents to clean plastic or rubber parts should be avoided if possible.

Ester-based cleaning agents which are available commercially have higher flash points and much lower vapor pressures than other available organic hydrocarbons. Most have low orders of toxicity, as well. The combination of these features makes esters excellent choices for use in formulated cleaning agents.

## Solubility Theory

Now that we have discussed the various classes or types of solvents in detail, the next question that we ask ourselves is, which solvent class or which specific solvent is the best choice for dissolving the soils that I have on my parts? In the past, kauri-butanol values have been assigned to solvents and used to measure their relative solvent power. The kauri-butanol scale is a linear one and provides a limited amount of information as to the relative solubilities of various classes of compounds.

It may be more appropriate to think of solubility as somewhat more complex than as a point on a linear scale. It can be viewed as a circle in a two dimensional plot or even as a sphere in a three dimensional plot. As the old saying goes "like dissolves like," but solubility cannot necessarily be characterized as yes or no. It's more correct to say that things which have similar "regions of solubility" tend to be good solvents for one another.

In the past few years, Hansen solubility theory has become accepted as a means of characterizing the relative solubility of various compounds. For any unique chemical compound, Hansen solubility theory assigns three solubility parameters which can be plotted in a three dimensional graph. Cleaning agent companies like DuPont have developed proprietary programs which allow them to assign solubility parameters or regions of solubility to complex soils such as metalworking fluids and grease. It also allows one to predict the effect of particular formulations on plastics and elastomers.

Once the solubility regions of the soils are plotted, it becomes a rather simple matter to select a solvent which falls near or within the solubility region for the soil. Often times, however, there is not one particular solvent which falls neatly within the solubility region for a given soil, or if one does fall within the solubility region, it may have some other characteristic which makes it unsuited for use in a manufacturing environment.

This theory has been used to develop formulated solvents. These are products with solubility characteristics similar to broad categories of soil but which are formulated from commercially available ingredients that have no significant toxicity or use concerns. If one can plot various base solvents on a two dimensional map, then a simple mixing rule can be applied in order to identify a combination of solvents which probably has the solubility characteristics necessary to dissolve particular classes of soils.

The use of this technology to develop cleaning agents specific for each individual application would be expensive and time consuming. But generally, the metalworking industry uses a few classes of relatively similar fluids (stamping oils, coolants, cutting oil, lapping compounds etc.). Carefully selected cleaning agents can be used to clean dozens or hundreds of individual soils within one of these categories. These formulated solvents have been developed from mixtures of compounds discussed above, and they have interesting and unique solubility characteristics designed to address specific and demanding classes of cleaning applications.

Individual solvent manufacturers are the best sources of information on which formulated solvents are available and which particular types of soils they will dissolve. As in many things, when selecting a formulated solvent, it is best to deal with a reputable solvent chemical supplier that has a variety of products and the technical resources to evaluate your application and support your system after it's operational.

## Solvent Cleaning Processes

Cleaning with hydrocarbon-based solvent cleaning processes can still be a very economic, efficient way to clean parts, particularly metal parts. The processes are often very simple. Sometimes they can be adapted to existing equipment or they can be implemented at lower capital cost than other processes. They can take less space and use less energy than aqueous, semi-aqueous or other types of cleaning processes, and there are generally no water issues. Finally, waste disposal costs for nonhazardous hydrocarbon cleaning agents are often lower than for other types of liquid waste.

Yes, any user with a hydrocarbon cleaning process will have to consider the VOC implications of the process, but with the development of advanced drying techniques and the introduction of formulated low-vapor-pressure hydrocarbons and other organic solvents, the VOC emissions from a hydrocarbon-based solvent cleaning process can be minimized and can be held at a level which is acceptable in virtually all states and local municipalities in the United States.

The first question that you need to ask yourself when identifying a process is "what am I trying to accomplish?" What does my part need to look like when I am done? You may not have to answer this question by saying it needs to look like it did when it came out of my vapor degreaser.

Years ago, vapor degreasing processes were installed in various areas of manufacturing plants because the solvents were inexpensive, the equipment was simple and compact, and the process was easy to operate and not very energy intensive. These vapor degreasing processes had the added benefit of delivering extraordinarily clean parts on a very reliable basis. These parts were often cleaner than they actually needed to be given the manufacturing environment in which they were being used. Parts which are going on to downstream manufacturing and will again be exposed to oil, grease and other contaminants may not need to be cleaned to the degree of cleanliness provided by chlorinated solvents. So, please keep in mind that when selecting a solvent cleaning process, consider what is going to happen to the part immediately after the cleaning step. This will be particularly important when identifying the drying requirements for the part.

There are several key elements of the solvent cleaning process that need to be considered. These elements include the temperature and type of agitation in the main wash bath, the soil concentration that can be tolerated in the main wash bath and in the rinse baths, the type and number of rinse sections that will be used on the machine and the drying process that is used. The following is a detailed treatment of each of these key process considerations.

## Agitation and Temperature

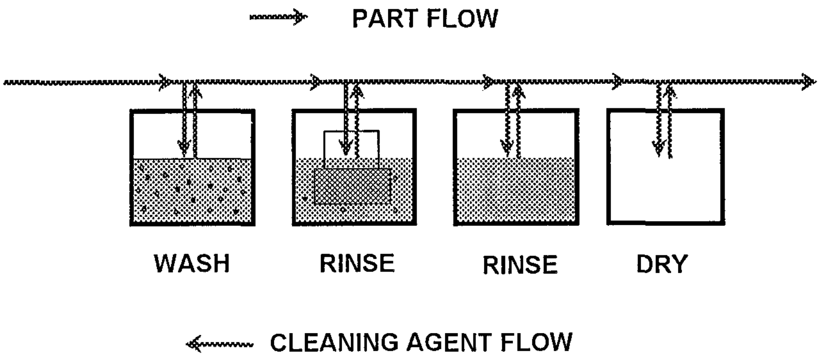
Agitation and temperature are two key elements of dissolving a soil into a cleaning agent. Remember that the goal in a solvent cleaning process is to dissolve the soil. Generally, the more agitation that is used or the higher the temperature in the cleaning bath, the faster the soil will be dissolved. Common types of agitation include, spraying, ultrasonic cavitation or moving a part which is submerged in a cleaning agent. Higher temperature may also improve the ultimate soil loading capacity of the solvent, that is, how much soil can be dissolved into the solvent before further dissolution of soil is not possible. In general, anything that is done with a solvent bath which increases the agitation intensity or the temperature will also increase the VOC emissions from the bath, so the agitation and temperatures for the process must be carefully selected to achieve the necessary results without going too far.

When heating a solvent, the user cannot ignore the safety implications of heating a material which has a flash point in the flammable (less than 100°F) or combustible (100°F to 140°F) range. Care must be taken to ensure that the heating process has redundant interlocks or safety systems built in which will prevent the solvent from reaching its flash point. These interlocks may not be necessary if the equipment is specifically designed to handle solvents which are at or above their flash point temperatures.

## Process

Hydrocarbon immersion cleaning uses an initial hydrocarbon wash tank, followed by one or more rinse tanks containing progressively cleaner solvent. These tanks are normally connected so that as fresh solvent is added to the final rinse tank, the overflow cascades through the other tanks toward the wash tank. The dirtiest solvent overflowing from the wash tank is disposed of or, potentially, recycled. The contaminant level in the final rinse tank defines ultimately how clean the part will be. The contaminant level in the final rinse tank is determined by the number of rinse tanks, the rate that fresh solvent is introduced into the final rinse and the rate at which contaminants are entering the wash tank. Any contaminant in the final rinse hydrocarbon will, in effect, be re-deposited on the part as the thin residue layer of hydrocarbon dries after it is removed from the last tank.

**HYDROCARBON IMMERSION**
**CLEANING SYSTEM**



## Drying

Because hydrocarbons have much higher boiling points than CFC-113 or methyl chloroform cleaners, parts removed from hydrocarbon immersion cleaning systems dry more slowly than those cleaned in halogenated solvents. Techniques to accelerate hydrocarbon drying have been developed and designed into equipment.

The degree of dryness needed depends on the processing steps that follow cleaning. Techniques are available that remove the hydrocarbon so as to leave the surface totally dry, or just dry to the touch. In some instances, drying may not be needed. The size of the equipment required, as well as the elapsed time, manpower, and energy expended, changes significantly with the degree of surface dryness required. Therefore, drying parts beyond the degree needed wastes time and money.

For example, during a machining operation, drying may not be necessary if the part was cleaned primarily to remove metal chips, fines and excess cutting oil before moving on to further machining. Complete drying may not be necessary if the part was cleaned only to check its dimensions and then returned for additional processing. In cases where parts are to be stored and not used for a while, they can be allowed to dry slowly. In fact, the remaining hydrocarbon cleaning agent may provide corrosion protection. In this case, simply allowing the hydrocarbon to drain off the parts is usually sufficient.

Parts may only need to be dry to the touch if the next processing step involves, for example, assembly, handling, packaging, inspection, or even painting with oil-based paint. This could be accomplished by spinning parts in a centrifugal dryer, blowing off the hydrocarbon with high velocity air knives, or vacuuming the liquid off the part.

Sometimes totally dry parts may be required, meaning 100% of the cleaning agent has to be removed. This can be accomplished by a forced hot air oven or vacuum dryer. A special hot air dryer called a "Class A" dryer should be used since it is designed to be operated in a way that prevents the vapor concentration of the combustible hydrocarbons from exceeding 25% of their lower explosive limit (LEL). Another means of accomplishing this is with a vacuum oven or an oven that uses a combination of heat and vacuum. In either case, the efficiency of these processes can be improved by removing as much excess cleaning agent as possible before the part enters the evaporative dryer.

## Equipment Retrofit

In many cases, vapor degreasers that are designed for use with CFC-113 and MCF can be modified for use with hydrocarbon cleaning agents. While it is preferable to use equipment that is specifically designed for immersion cleaning with hydrocarbons, modifying a vapor degreaser can be effective for extended testing, or for use until new equipment is available.

The retrofit process first involves rendering the equipment safe for use with hydrocarbons. This includes disconnecting or removing electrical heating elements and, adding additional ventilation. The old condensing coils should also be removed to ensure the unit is not mistaken for or used as a vapor degreaser.

Other alterations can be made to enhance cleaning, such as adding filtration and agitation. If the hydrocarbon cleaning agent has a high enough flash point, heating can be added, preferably using a hot water coil or plant steam.

## Waste Disposal

Although waste disposal is not a primary part of the actual cleaning process, it can play an important part in the overall economic viability of the cleaning process. Waste disposal is often one of the most important advantages of hydrocarbon or solvent cleaning processes over water and chlorinated solvent processes. Organic cleaning agents are generally hazardous waste only if their flash point falls below 140°F, and as was discussed earlier, there have recently been introduced several high quality, very effective cleaning agents with flash points over 140°F. Even if it is necessary to use a solvent with a flash point below 140°F, these solvents are generally less expensive to get rid of than water and chlorinated wastes. Several large reputable solvent distributors have excellent waste disposal programs.

Solvent users also need to keep in mind that while a particular solvent may not be a hazardous waste in and of itself, the user may render the waste hazardous by adding something to the solvent. When cleaning petroleum based metalworking fluids, this should not be a problem. Waste solvent should be filtered to remove metal chips and fines. Also, take care to ensure that water or water-containing wastes are not mixed with the hydrocarbons, and finally, do not mix wastes with widely varying flash points. Don't try to add some low-flash waste to your non-hazardous cleaning agent waste. You may do nothing more than reduce the flash point of the entire blend.

If a particular solvent user wishes to engage in waste minimization and reduce the overall volume of waste generated in their plant, waste hydrocarbon solvents can be vacuum distilled under some circumstances. In general, however, these vacuum distillation processes are less economically justified for organic hydrocarbon solvents than they are for chlorinated materials. The hydrocarbons tend to have higher boiling points and are somewhat more difficult to vacuum distill. Also, their low purchase cost and relatively low disposal cost does not usually justify the capital expenditure required for installing a complicated vacuum distillation system.

## Conclusion

There is still a very significant place for organic solvent cleaning processes in today's manufacturing environment. The advent of formulated products has produced cleaning agents with broad ranges of cleaning capability, like that of the chlorinated solvents. The equipment in which these cleaning agents can be used tends to be simpler and less expensive than other types of equipment available on the market today. Drying is the major drawback of cleaning using hydrocarbon immersion solvents, but the user will always have the opportunity to choose between the engineering controls required to implement volatile hydrocarbon solvents, which dry faster and even more efficiently than water, or he can put in complex, efficient drying systems which can dry even the least volatile high flash point hydrocarbon solvents.

Waste disposal of hydrocarbon solvents also tends to be less expensive than waste disposal issues for other water and chlorinated solvent based materials.

Solvent is ***not*** a four-letter word. Safe, efficient, cost effective organic solvent cleaning processes are in use all over the world. If you need to change or modify your cleaning process, organic solvents should be carefully considered along with all the other cleaning technologies available today.

## Acknowledgments

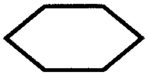
I would like to personally thank several of my colleagues for their contributions to this paper. Thank you to Dr. Mike Hayes, Beth Bivins and Al Wood at Petroferm for their assistance in the writing and editing of this work, and to Dr. John Durkee for review and comments on the final text.

# Appendix 1.

**Saturated Hydrocarbon**

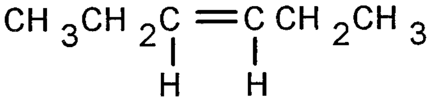
$CH_3CH_2CH_2CH_2CH_2CH_3$

n-Hexane



Cyclohexane

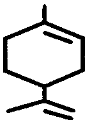
**Unsaturated Hydrocarbon**



$$CH_3CH_2\underset{\substack{|\\H}}{C}=\underset{\substack{|\\H}}{C}CH_2CH_3$$

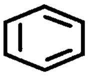
3-Hexene

**Terpene**

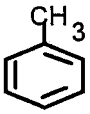


Limonene

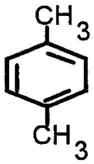
**Aromatic Hydrocarbons**



Benzene

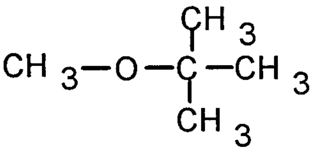


Toluene



Xylene

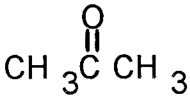
**Ether**



$$CH_3-O-\overset{CH_3}{\overset{|}{\underset{\substack{|\\CH_3}}{C}}}-CH_3$$

MTBE

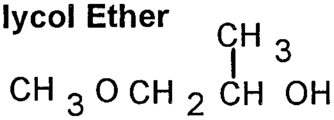
**Ketone**



$$CH_3\overset{O}{\overset{\|}{C}}CH_3$$

Acetone

**Glycol Ether**



$$CH_3OCH_2\overset{CH_3}{\overset{|}{C}H}OH$$

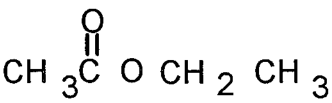
Propylene Glycol Methyl Ether

**Alcohol**

$CH_3CH_2OH$

Ethanol

**Ester**



$$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$$

Ethyl Acetate

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