

Besides being used as a circulator, a pump of design similar to Figure 9 was used as a compressor to 6000 pounds per square inch. For this use, and with lubricant introduced in the line immediately before the intake valve, the pump behaved perfectly. In this case, cooling for the cylinder was provided by means of a water jacket. This pump maintained 6000 pounds gas pressure for a period of 24 hours, without loss discernible on a Bourdon tube gage graduated in 100-pound units.

Magnetic Regulating Valve

It frequently is more advantageous to run an experiment from gas in storage than direct from a compressor. In such a case the stored gas would necessarily be at a pressure considerably higher than the operating pressure. With a valve as shown in Figure 10 in the line, the pressure on the test can be maintained constant.

The valve, described more fully in a previous⁷ paper, consists of an electromagnet and a needle valve. The core, being magnetized by the closing of the circuit, pulls the valve off its seat, admitting gas from the pressure side. A break in the circuit causes the core to lose its magnetism, releasing the valve which is reseated by the valve spring. The operation of the valve is controlled by the gage, in which the circuit is completed by contact between the Bourdon tube and an adjustable contact point.

With a desired operating pressure of 200 atmospheres, it can be assumed that the entering gas is at 300 atmospheres and the valve is open. When the pressure on the discharge side of the valve reaches 200 atmospheres, contact is made between the Bourdon tube and the adjustable contact point.

⁷ Larson and Karrer, *THIS JOURNAL*, **14**, 1012 (1922).

This closes the circuit, magnetizing the relay, thus breaking the secondary circuit, releasing the valve which shuts off the flow of gas. As the pressure on the discharge side of the valve drops to 200 atmospheres, minus a small increment dependent upon the sensitivity of the Bourdon tube, the preliminary circuit is broken and the relay is demagnetized, which closes the circuit of the secondary system. The electromagnet of the valve is magnetized and pulls the valve off its seat, admitting high-pressure gas through the valve to the operating equipment. This completes the cycle, which might be repeated as often as once per second. Regulation by this means can be so close that a recording pressure gage shows no fluctuation in pressure.

This valve has other applications, one of which is in the bypass line of a compressor between the discharge and intake, where a constant delivery pressure is desired.

High-Pressure Relief Valve

In working with gases at these higher pressures, it is very necessary for both safety of person and of equipment to have dependable relief valves in the line. "Pop" valves, which will relieve at a set pressure, but which will not reseal again and maintain the operating pressure, can be secured commercially. Such a valve is satisfactory as a safety valve, but is wasteful in both time and gas, as after relief the contained gas must escape before the valve can be taken down and reseated. A high-pressure relief valve that will relieve and reseal again at the operating pressure has been developed at the Fixed Nitrogen Research Laboratory. This valve (Figure 11) is described more fully elsewhere.⁸

⁸ Ernst and Reed, *Mech. Eng.*, **48**, 595 (1926).

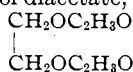
The Glycol Ethers and Their Use in the Lacquer Industry¹

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IN APPRECIATION of the growing importance of the lacquer industry, a study of the derivatives of ethylene glycol was begun a number of years ago with a view toward the development of new solvents for cellulose esters.

The state of the art as then developed indicated that esters were the best nitrocellulose solvents, and accordingly the first solvents produced were of this type. Glycol diacetate, having the formula

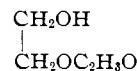


is an example of the products developed at this time. It is an excellent solvent both for cellulose nitrate and cellulose acetate, Table IV, but its boiling point, 186° C., is somewhat higher than ordinarily is desired. Other glycol esters fell into the same class, and since lower boiling solvents were

The ether derivatives of the alkyl glycols are good solvents for cellulose esters. These ethers are all practically odorless, which is important in the manufacture of lacquers for use in interior work.

The monoethyl ether of ethylene glycol is a more powerful solvent for nitrocellulose and stands dilution with nonsolvents better than any solvent of comparable boiling range that has been examined. Indirectly, the use of this solvent makes possible the production of a lacquer that has better hiding and covering power, minimizes the tendency to "brush through" when used for second and third applications, and reaches its permanent hardness quickly.

desired the study of this type of solvent was discontinued and the experimental work was extended to the two-type solvents. The first development in this direction was glycol monoacetate



which is a mixed alcohol-ether. This compound is a reasonably good solvent for cellulose esters, but its boiling

point, 181° C., is also somewhat high, and other alcohol-ether combinations were open to the same objection.

For many years a mixture of alcohol and ether has been recognized as an excellent solvent for cellulose nitrate, and it was therefore thought that a mixed alcohol-ether derivative of ethylene glycol might have interesting solvent properties in this same direction.

The monoethyl ether of ethylene glycol was the first compound of the ether-alcohol type prepared. Its boiling point was in the desired range and it proved to be such a powerful solvent for cellulose nitrate that the work was extended to

¹ Presented under the title "Glycol Ethers as Solvents for Cellulose Esters" before the New York Section of the American Chemical Society, New York, N. Y., May 7, 1926.

cover other ethers of ethylene glycol and later was expanded to a study of the ethers of propylene and still higher glycols. This study is still in progress and, as far as the work has progressed at present, all compounds falling in this class are excellent nitrocellulose solvents.

Monoalkyl Glycol Ethers

Table I summarizes the physical properties of the most important ethers studied.

Table I—Physical Properties of the Monoalkyl Ethers of Ethylene and Propylene Glycols

Monoalkyl Ether	Boiling point ^a ° C.	Specific gravity 15°/15° C.	Refractive index (n_D) at 26° C.
<i>Ethylene Glycol</i>			
Methyl	124.5	0.9748	1.4004
Ethyl	134.8	0.9360	1.4042 (24° C.)
Isopropyl	144.0	0.9139	1.4080
<i>n</i> -Propyl	150.0	0.9110	1.4125
Isobutyl	158.8	0.9130	1.4135
<i>n</i> -Butyl	170.6	0.9188	1.4177
Isoamyl	181.0	0.9000	1.4198
<i>Propylene Glycol</i>			
Methyl	122.8	0.9335	1.4035
Ethyl	133.0	0.9090	1.4061
Isopropyl	141.5	0.8900	1.4062
<i>n</i> -Propyl	150.0	0.8970	1.4102
Isobutyl	161.3	0.8810	1.4112
<i>n</i> -Butyl	170.6	0.8890	1.4151
Isoamyl	183.3	0.8835	1.4182

^a Boiling point of monoalkyl ethers of ethylene glycol at 743 mm. pressure, of propylene glycol at 736 mm.

All these compounds are colorless, mobile liquids and are practically without odor, a very desirable property for an ingredient of lacquers. They are good solvents for nitrocellulose and the methyl ether derivatives, at least for ethylene and propylene glycols, are also excellent solvents for cellulose acetate.

In general, they are good solvents for resins, oils, and gums, the solubility for these materials increasing somewhat as the boiling point of the ether increases. (Table IV.) They are completely miscible with most organic solvents. The lower ethers are also soluble in water. In general, the solubility curves with respect to water are closed rings, which indicates that within certain temperature limits these compounds are less soluble in hot water than in cold. Only a few points on the curves of the lower members can be determined at ordinary temperatures, but the complete curves for the butyl and isobutyl ethers of ethylene glycol have been plotted by Cox and Cretcher.² These two compounds show both upper and lower consolute points within the ordinary temperature zones.

It will be noted from Table I that the boiling points and refractive indices increase, but the specific gravity decreases, as the molecular weight of the ether radical increases. The boiling points of the propylene glycol ethers very closely approximate the boiling points of the ethylene glycol ethers, and their solvent properties are almost identical. The work on butylene and still higher glycol derivatives is not yet completed, but preliminary investigations indicate no very decided variations from the properties of the ethylene glycol derivatives.

All of the ethers have not been studied completely, but the ethyl and methyl ethers, at least, form constant boiling point mixtures with water, the ethyl ether, for example, forming a mixture that contains approximately 40 per cent of the ether by volume and boils at 98–99° C.

The dilution ratio of the ethers is unusually high, ranking above ethyl lactate in this respect and exceeding the dilution ratio of butyl acetate by more than 200 per cent. A summary of these dilution ratios determined with respect to toluene,

and to water is given in Table II. The data were determined by dissolving 2 grams of nitrocellulose in 20 cc. of solvent and diluting the mixture with toluene, gasoline, or water until the nitrocellulose precipitated. This volume, divided by the volume of solvent originally used (20 cc.), represents the dilution ratio.

Table II—Dilution Ratios
For Cellulose Nitrate

SOLVENT	Toluene	Gasoline	Water
Ethylene glycol monoethyl ether	6.25	1.50	0.35
Ethyl lactate	5.25	0.75	0.27
Propylene glycol monoethyl ether	5.00	1.00	0.30
Ethylene glycol monomethyl ether	4.75	0.50	0.25
Ethylene glycol monopropyl ether	4.25	1.75	0.35
Ethylene glycol monoisopropyl ether	4.25	1.50	0.32
Ethylene glycol monobutyl ether	4.00	2.25	0.375
Methyl lactate	4.00	0.25	0.25
Mesityl oxide	3.75	0.75	0.05
Diacetone alcohol	3.25	0.50	0.22
Ethylene glycol monoisoamyl ether	3.00	2.25	0.10
Ethylene glycol monoisobutyl ether	2.75	1.75	0.20
Butyl acetate	2.75	1.00	0.00
Propylene oxide	2.50	0.75	0.15
Butyl propionate	2.50	0.75	0.00
Secondary butyl acetate	2.00	1.00	0.00
Secondary amyl acetate	2.00	1.00	0.00
Secondary hexyl acetate	1.75	0.75	0.07
Glycol diacetate	1.75	0.25	0.10
Diethylene oxide	0.25	0.25	0.27
<i>For Cellulose Acetate</i>			
Ethylene glycol monomethyl ether	1.25	0.25	0.15
Ethyl lactate	1.25	0.25	0.15
Glycol diacetate	0.75	0.25	0.00

Ethyl lactate, methyl ether of ethylene glycol, methyl lactate, mesityl oxide, diacetone alcohol, and glycol diacetate solutions did not precipitate nitrocellulose with gasoline at the ratios given, but two layers formed on further addition of gasoline.

Derivatives of the Glycol Alkyl Ethers

A number of derivatives of the glycol ethers have also been studied. For example, the diethyl and dimethyl ethers of ethylene and propylene glycols have been prepared and solvents of the ether-ester type such as the acetate of ethylene glycol monoethyl ether have been made. Neither type, however, was as generally useful as the alcohol-ether combinations.

The diethyl ether of ethylene glycol is a liquid of faint odor, boiling at 121° C. having a refractive index of 1.3914 and a specific gravity of 0.853. As might be expected from its composition, it is considerably less soluble in water than the monoethyl ether. It dissolves cellulose nitrate but not the acetate (see Table IV for its action on gums and resins).

The acetate of ethylene glycol monoethyl ether is only partially soluble in water. It is a liquid boiling at 153° having a specific gravity of 0.982 at 18° C. Owing to the inclusion of the acetate group, it has a stronger odor than the simple monoalkyl ethers. It dissolves both cellulose nitrate and cellulose acetate. A summary of its solvent properties is given in Table IV.

Table III—Physical Properties of Some Polyglycols and Their Ethyl Ether Derivatives

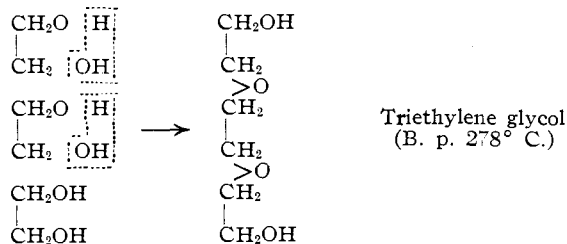
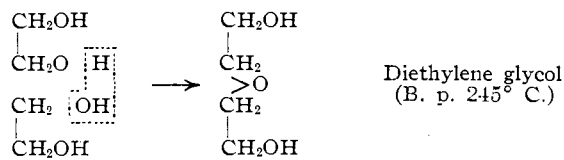
COMPOUND	Boiling point (760 mm.) ° C.	Specific gravity 15°/15° C.	Refractive index (n_D) at 26° C.
Diethylene glycol	245	1.132 (0° C.)	
Triethylene glycol	276	1.138	
Tetraethylene glycol	230 (25 mm.)		
Diethylene glycol monoethyl ether	198	0.9996	1.4240
Triethylene glycol monoethyl ether	248	1.0566	1.4389
Tetraethylene glycol monoethyl ether (approx.)	284	1.4389	1.4499

Polyglycols and Their Derivatives

By the elimination of a molecule of water from two molecules of glycol, a polyglycol may be formed; and by the elimination of an additional molecule of water from this polymer

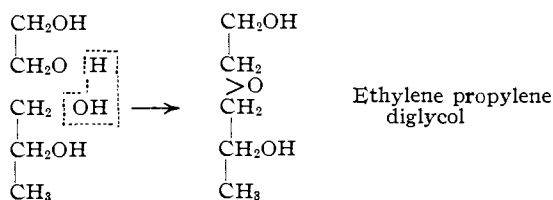
² *J. Am. Chem. Soc.*, **48**, 451 (1926).

and another molecule of glycol, a still higher polymer will be produced. For ethylene glycol the reactions may be presented as follows:



This reaction can be greatly extended and polyglycols as high as decaethylene glycol have been prepared.

It is also possible to produce mixed polyglycols; thus, with ethylene and propylene glycols, the following reactions take place:



Owing to the inclusion of the ether group, all of these polyglycols are good solvents for cellulose esters, gums, and resins, the best effect being produced when the ether and alcohol groups are evenly balanced. Thus, triethylene glycol, containing two hydroxyl and two ether groups, seems to be a somewhat better solvent than either diethylene glycol, containing two hydroxyl groups and one ether group, or pentaethylene glycol having two hydroxyl groups but four ether groups.

On account of the presence of the two hydroxyl groups, the polyglycols are very hygroscopic, ranking with glycerol in this respect, but this property, ordinarily considered a liability in a nitrocellulose solvent, does not seem to affect their solvent properties greatly. In fact, there are many special uses for such solvents, particularly in the production of plastics such as motion picture film and celluloid, where their incorporation gives increased pliability and makes possible the retention of flexibility even in dry atmospheres.

The hydroxyl groups of the polyglycols can readily be exchanged for ether groups and there are therefore a whole series of mono- and dialkyl ethers for each polyglycol.

The alkyl ether derivatives of the polyglycols have boiling points approximately 15° to 40° C. lower than the poly glycol from which they are derived, and in the case of the ethyl ethers that have been studied the boiling points almost exactly correspond with the next lower polyglycol. They are not particularly hygroscopic and have already been used with success as plasticizers in lacquers. Both the polyglycols and their ether derivatives are practically odorless. (Table III)

Cyclic Ether Derivatives of the Glycols

The elimination of a molecule of water from a single molecule of glycol instead of from two, as in the formation of the

Table IV—Solubility of Various Solvents on Cellulose Nitrate and Acetate, Resins, Gums, and Common Diluents

	Water	Cellulose nitrate	Cellulose acetate	Linseed oil	Casoline	Kerosene	Toluene	Benzene	Shellac	Gum kauri	Gum copal	Gum sandrac	Gum mastic	Gum guaiac	Gum dammar	Gum camphor	Gum cumarone	Gum zanzibar	Gum elemi	Japan wax	Rosin "E"	Ester gum
Amyl acetate	i	s	i	s	s	s	s	ss	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Amyl alcohol	ss	i	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Butyl acetate	i	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Butyl alcohol	ss	i	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Butyl butyrate	i	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Glycol ether acetate	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Diacetone alcohol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Dichloroethyl ether	i	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Ethyl acetate	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Ethyl alcohol	s	i	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	s	s	s	s	s
Ether	i	s	i	s	s	s	s	s	ss	ss	s	s	s	ss	s	s	s	s	s	s	s	s
Ethers of ethylene glycol:																						
Methyl	s	s	s	i	s	s	s	s	s	s	s	s	s	s	p	s	i	ss	s	s	s	ss
Ethyl	s	s	s	s	s	s	s	s	s	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Diethyl	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Propyl	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Isopropyl	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Butyl	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Isobutyl	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Isoamyl	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	ss
Ethers of propylene glycol:																						
Ethyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	s	i	s
Methyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	s	i	s
Isopropyl	s	s	i	s	s	s	s	s	s	s	g	s	s	ss	p	s	s	ss	s	s	i	s
Glycol diacetate	i	s	s	i	i	i	s	s	i	i	i	i	i	i	i	i	i	i	i	i	i	i
Diethylene oxide	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Isopropyl acetate	ss	s	i	s	s	s	s	s	ss	s	s	s	s	ss	p	s	s	ss	s	s	s	s
Propylene oxide	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Ethylene oxide	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Butyl propionate	i	s	s	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	s
Glycol monoacetate	s	s	s	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	s
Diethylene glycol monoacetate	s	s	s	s	s	s	s	s	ss	s	s	s	s	ss	p	s	s	ss	s	s	s	s
Diethylene glycol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	s
Triethylene glycol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	s
Tetraethylene glycol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	s	s	s	ss	s	s	s	s
Ethyl ether of:																						
Diethylene glycol	s	s	i	s	s	s	s	s	s	s	s	s	s	ss	p	s	s	ss	s	s	i	s
Triethylene glycol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	p	s	s	ss	s	s	i	s
Tetraethylene glycol	s	s	i	s	s	s	s	s	ss	s	s	s	s	ss	p	s	s	ss	s	s	i	s
Butyl ether of diethylene glycol	s	s	i	s	s	s	s	s	ss	s	g	s	s	ss	p	s	s	ss	s	s	i	s

Key
 s — Soluble g — Swells
 ss — Slightly soluble p — Partially soluble
 i — Insoluble

polyglycols, results in the formation of a cyclic ether, usually called an oxide.

In this way ethylene, propylene, and butylene oxides may be produced from their respective glycols. These oxides are very powerful solvents, dissolving cellulose nitrate, acetate, and ether with avidity. They are soluble in water and are almost odorless. Ethylene and propylene oxides, having the respective boiling points of 10.5° and 35.0° C., are too volatile for general use, but the higher boiling oxides should prove important industrial solvents.

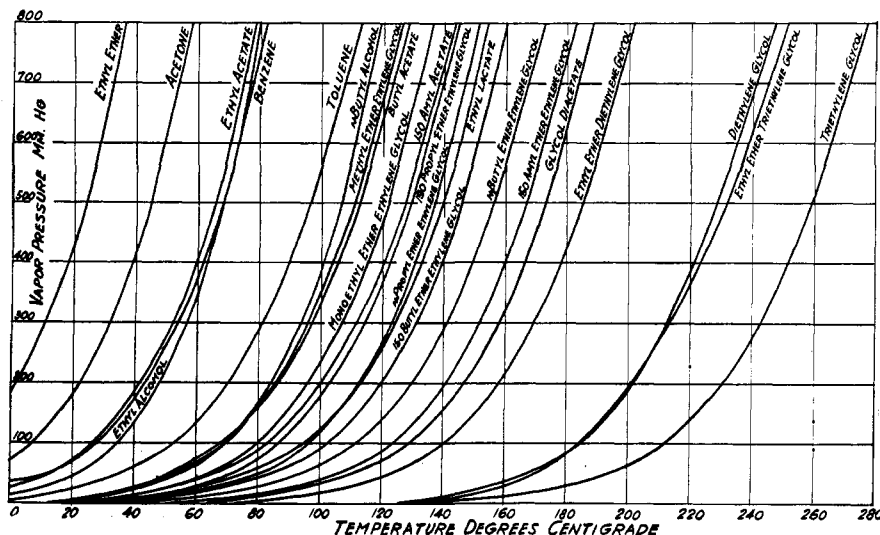
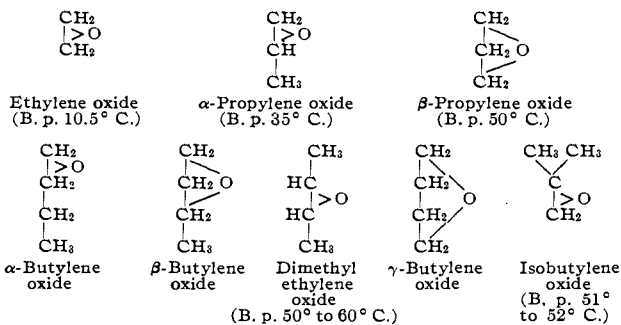
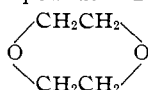


Figure 1—Vapor Pressure of Organic Solvents

Only one ethylene oxide is possible, but two propylene and five butylene oxides have been produced. These have the formulas indicated below:



The simple oxides may be polymerized with the production of more complicated compounds. Thus diethylene oxide



or 1,4-dioxan, may be produced by the polymerization of ethylene oxide with caustic or by distilling ethylene glycol with phosphoric acid. It is a liquid of faint odor, soluble in water, and boiling at 102° C. It is a fair solvent (Table IV) for cellulose esters and resins.

It is obvious that a whole series of cyclic ethers varying in complexity and properties but having the same general characteristics may be prepared from the corresponding glycols or from the simple oxides. An investigation of their properties is now in progress.

Vapor Pressure and Rate of Evaporation

Once it has been determined that the liquid under investigation is a solvent for cellulose nitrate and compatible with

gums, the vapor pressure and the rate of evaporation are of value in determining how the solvent will act in a lacquer. Figures 1 to 7 summarize in graphic form the findings for a number of nitrocellulose solvents.

The vapor pressures as shown in Figures 1 and 3 were plotted from actual experimental determinations by the dynamic method. Figures 2 and 4 were produced by replotting the data on paper which has a logarithmic scale for the ordinates and a descending harmonic scale for abscissas. The logarithms of the vapor pressures were plotted against the reciprocal of the absolute temperatures

which, in accordance with the modified form of the Clapeyron-Clausius equation, $\text{Log } P = \frac{-K}{T}$, gives a curve that is almost a straight line. This method of plotting permits the vapor pressures of the solvents to be quite accurately compared at temperatures approximating those under which lacquers are allowed to dry in use.

Examination of Figures 1 and 2 shows that ethylene glycol monomethyl ether, ethylene glycol monoisopropyl ether, and ethylene glycol monopropyl ether have vapor pressure curves closely approximating the respective curves of butyl acetate, amyl acetate, and ethyl lactate. Ethylene glycol monoethyl ether itself lies between butyl acetate and amyl acetate. In Figure 2 the relative vapor pressures of these solvents are quite different at low temperatures from the relationships that exist at high temperatures, and in three cases the position of the solvents is reversed. At 25° C. ethylene glycol monoethyl ether has almost exactly the same vapor pressure as amyl acetate. Water has a greater vapor pressure than toluene at temperatures above 52° C., but this condition is decidedly reversed at lower temperatures.

Figures 3 and 4 show the relative vapor pressures of a number of plasticizers including several polyglycols and their monoethyl ether derivatives. Figure 4 was plotted in the same manner as Figure 2, and since the vapor pressure of the plasticizers at ordinary temperatures is very low, this method of comparison is of particular importance for this type of solvent.

The curves in Figures 5 to 7 were determined by allowing 2 grams of solvent to evaporate in an open tin can top $\frac{1}{2} \times 3$ inches at ordinary room temperatures. The values obtained by this method are not absolute and cannot be checked from day to day, but a relationship between various solvents can be worked out in this manner. Figure 6 indicates that ethylene glycol monoethyl ether evaporates more slowly than butyl or amyl acetates and very closely approximates the evaporation curve of butyl propionate. This property of ethylene glycol monoethyl ether has made possible the production of a brush lacquer that will dry slowly enough to permit all brush marks and inequalities of the lacquered surface to smooth out, but sufficiently fast to make the use of lacquers containing it feasible for domestic purposes. It will be understood, of course, that the low boiling diluents present will speed up the drying time considerably beyond that shown in Figure 6.

The vapor pressure and rate of evaporation for ethylene glycol monoethyl ether are almost ideal for the production of a surface of high gloss free from blemishes. Many of the defects of ordinary quick-drying lacquers such as "orange peel," streaking, and blushing can be overcome by the addition of glycol ethers selected with due respect to the desired drying qualities.

On the basis of the above information, it will be observed that the vapor pressure curves as usually determined are not entirely safe as indicators of the volatility of solvents. On the other hand, the evaporation curves are very difficult to check, and if carried out over extended periods of time, as

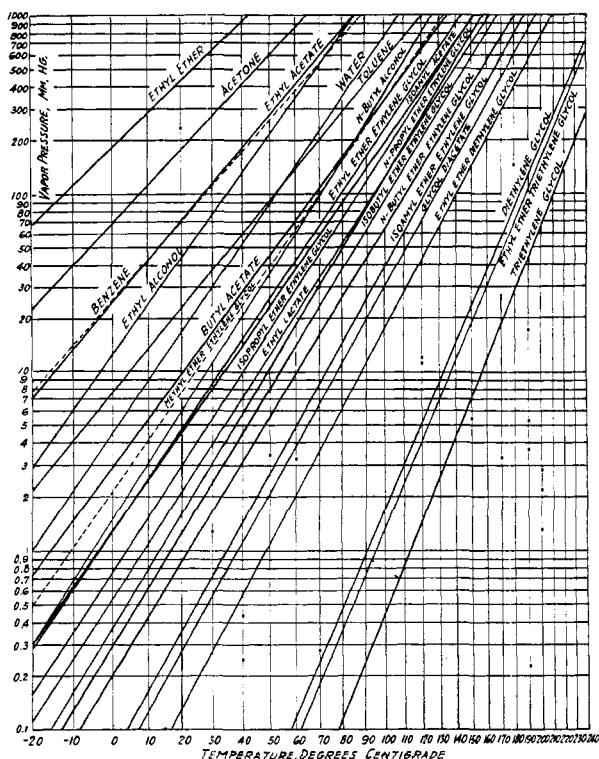


Figure 2—Vapor Pressure of Organic Solvents—Logarithmic Curves

becomes necessary in considering the higher boiling solvents, are subject to many outside influences.

The solution would seem to be a very accurate method of determining vapor pressures between 0 and 10 mm. pressure, giving proper consideration to the molecular weight and latent heat of evaporation.

It should of course be further remembered that the influence of other solvents and of nitrocellulose in the complete lacquer will further disturb the relationships indicated above.³

Importance of the Glycol Ethers in the Lacquer Industry

The development of the lacquer industry has been predicated, not upon the fundamental requirements of an ideal film, but principally upon the availability at reasonable cost of nitrocellulose solvents in the "medium boiler" class. The choice of solvents in this range has never been very large and until now has, for all practical purposes, been limited to a single ester.

An ideal solvent is one that will readily dissolve nitrocellulose and gums and render them compatible with each other. It must not evaporate so rapidly that "orange peel" or other surface defects will appear. It must permit high dilution with the cheaper nonsolvents such as toluene, and the addition of small amounts of water without pre-

cipitation of the nitrocellulose. It is also essential that the solvent will not hydrolyze with the production of acid, as this would have a deleterious effect upon the permanency of the film. Hydrolysis of the nitrocellulose solvent also has a very deteriorating effect if the lacquer must be stored for any period of time before use. The production of acid from this cause is very likely to change the character or consistency of the lacquer. It will affect the color and will give rise to a bad tarnish test if the lacquer is subsequently used on metals. Absence of residual odor, as has been indicated by many other authors, is very important.

In addition to the base solvent, lacquers should also contain another solvent of very high boiling point, this solvent ordinarily being referred to as the plasticizer. The plasticizer is not expected to evaporate from the film, its presence conferring the desired flexibility.

In Table IV a number of solvents, including the more important glycol ethers, have been tabulated with respect to their solvent effect on cellulose nitrate and acetate, resins, gums, and many of the common diluents.

An examination of the properties of the ether derivatives of the glycols shows that these compounds very closely approximate the ideal conditions set forth above. Ethylene glycol monoethyl ether, for example, is an excellent solvent for nitrocellulose and resins, and miscible in all proportions with most organic solvents. It has a higher dilution ratio than any solvent yet examined, with respect to the hydrocarbon diluents such as toluene, to gasoline, and to water. This means that ethylene glycol monoethyl ether solutions of nitrocellulose can be extensively diluted with nonsolvents, and films produced from these lacquers will not blush in drying owing to the ability of the solvent to absorb fairly large amounts of water. In fact, as would be expected from the dilution ratio, several per cent of water can be sprayed upon a film containing ethylene glycol monoethyl ether without causing precipitation of the nitrocellulose or resin. This water is finally eliminated through the constant boiling mixture with ethylene glycol monoethyl ether, which, it will be remembered, has a lower boiling point than water.

Since these solvents contain no ester group, it is impossible for them to develop acidity through hydrolysis. It is believed this lack of hydrolysis is partly responsible for the long

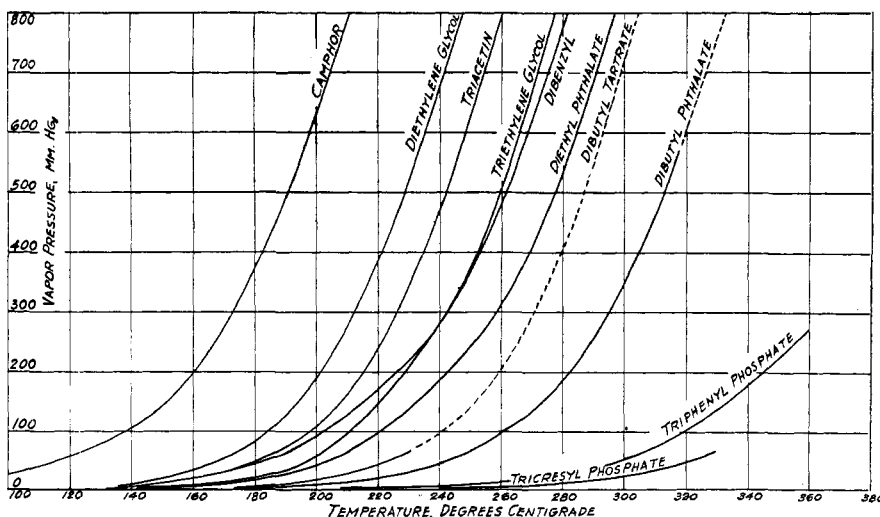


Figure 3—Vapor Pressure of Plasticizers

life of lacquer films produced from glycol ether solvents, and it is certain that the excellent keeping qualities of these lacquers in storage is due, at least in part, to the lack of hydrolysis. This is of particular importance in brush lacquers that

³ Gardner and Parks, *Paint Mfrs. Assoc., Tech. Circ.* 218.

are marketed in cans and which, through ordinary business channels may take, in particular instances, a year or more to reach the ultimate customer.

The odorless feature of ethylene glycol monoethyl ether and the other derivatives of the glycols makes their use in

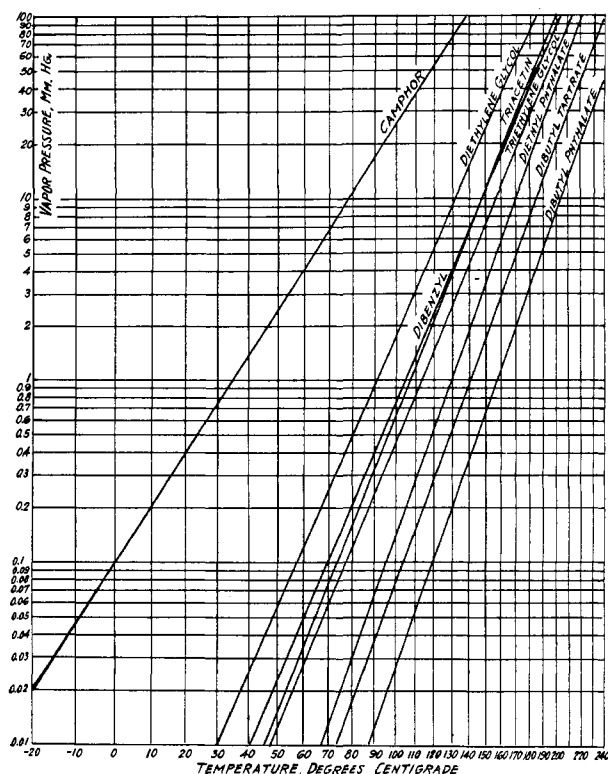


Figure 4—Vapor Pressure of Plasticizers—Logarithmic Curves

lacquers, particularly when the lacquers are to be used for inside work, very desirable. The objection to the use of lacquers in finishing the inside of kitchens, refrigerators, and bookcases because of the persistent and undesirable residual odor of butyl acetate is completely overcome. In fact, ethylene glycol monoethyl ether lacquers were first successfully used for this type of work.

Lacquers made from the glycol ethers are especially valuable for large-scale interior work involving the use of spray guns. Under ordinary conditions when the highly odoriferous butyl acetate is employed as the solvent, it is necessary for the workmen either to wear masks or leave their work every 15 to 20 minutes for a breath of fresh air. In contrast to this, a recent piece of work involving the use of ethylene glycol monoethyl ether lacquers in finishing the walls of a ten-room house showed that it was possible for the operators to carry on their work all day without interruption and without discomfort.

On the other hand, if it is only the trim and doors that are to be finished, brush lacquers made with glycol ether solvents can be brushed on as readily as enamel and, while drying more rapidly, result in a much better piece of work from the standpoint of hardness or resistance to abrasion, appearance, and texture than is generally possible with enamel. The lack of odor makes it possible to occupy refinished rooms as soon as the lacquer is dry, which for all practical purposes is within a half hour.

In view of the ease of application and the lack of residual odor, it would seem that the availability of lacquers based upon the glycol ethers will shortly bring about more general use of lacquers for the purpose of interior decoration.

The powerful solvent effect and the high dilution ratio of the

glycol ethers, taking ethylene glycol monoethyl ether again for an example, make it possible to keep considerably more nitrocellulose in a lacquer than when weaker solvents such as butyl acetate are used, in each case assuming desirable brushing fluidity to be retained. The unusually high content of nitrocellulose in turn allows the incorporation of greater than normal quantities of pigment and this results in a lacquer that has greater hiding and covering power than is otherwise obtainable. When butyl acetate is used as a solvent under these conditions, in order to obtain proper brushing qualities it is necessary to incorporate a large amount of plasticizer. The rate of solvent evaporation (for the example under discussion) is such that the lacquer film reaches its ultimate and permanent hardness very quickly. This is not true when butyl acetate and a plasticizer are used as solvents for, although the butyl acetate will evaporate very quickly giving the film and initial set, the plasticizer evaporates very slowly indeed. For this reason the film does not reach its permanent hardness for several days, or even weeks, and is therefore susceptible to abrasion or rapid wear over this period of time. Ethylene glycol monoethyl ether brushing lacquers do not require a high percentage of plasticizers and in fact they may be omitted entirely. Furthermore, the ability to incorporate abnormally large amounts of nitrocellulose in the glycol ether cited without the necessity of adding large amounts of plasticizers makes it possible to produce films in which the permanent hardness or resistance to abrasion is much greater than usual.

Whereas the glycol ethers in general, and the ethyl ether in particular, are very powerful solvents for nitrocellulose, they are somewhat slow in their action. Thus, a given quantity of nitrocellulose will require a longer time for complete solution than is the case when butyl acetate, for example, is the solvent. On the other hand, when the glycol ether is used as the nitrocellulose solvent in a brushing lacquer and successive coats of lacquer are applied over the original one, this slow action gives sufficient time to brush out the last coat, but owing to the slow solvent action it does not give

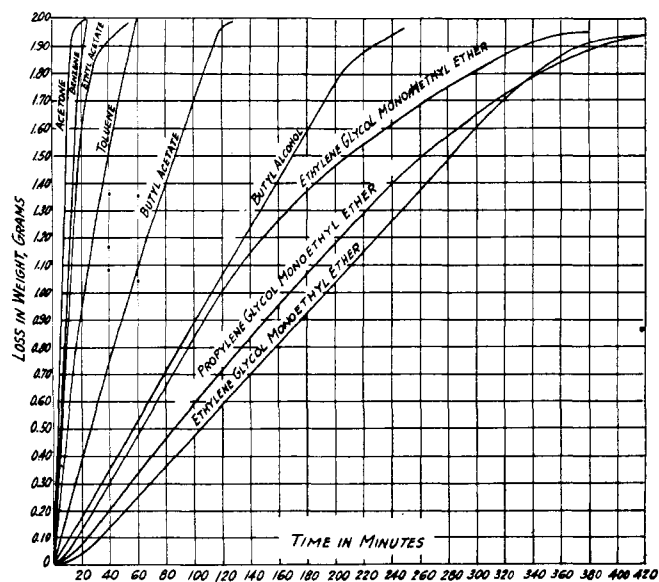


Figure 5—Evaporation Curves of Organic Solvents

Sample—2.00 grams. Container—Tin cover (3.25 in. diameter \times 0.5 in. deep)

sufficient time to cut through the previously applied coats. This point will be immediately appreciated by those who have endeavored to apply second and third coats of the usual type lacquers by means of a brush.

Summing up then, we find lacquers prepared with ethylene

glycol monoethyl ether as the nitrocellulose solvent have the following outstanding advantages:

- (1) Excellent brushing qualities.
- (2) Very great hiding power, which makes fewer coats necessary, thus increasing coverage.

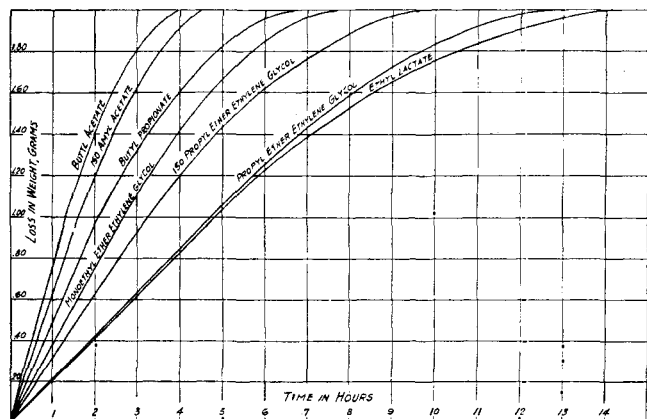


Figure 6—Evaporation Curves for Organic Solvents

- (3) Slow solvent action on previously applied coats, thus minimizing "brushing through" or "pick up."
- (4) Evaporates slowly enough to produce excellent gloss and finish, but fast enough to reach permanent hardness quickly.
- (5) Produces films that are harder and more resistant to abrasion than usual due to higher nitrocellulose content and to the fact that large amounts of plasticizers are not required for good brushing qualities.
- (6) No residual odor.

It must be remembered that the glycol ethers are in no respect substitutes for the solvents now commonly in use. They have fundamentally different properties and the criteria that have been applied to the older solvents will not exactly

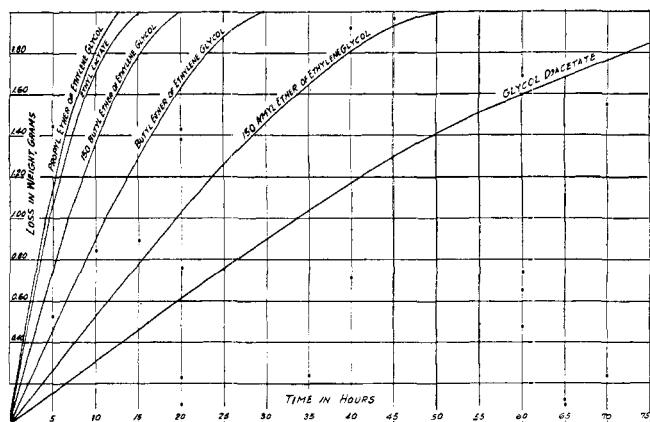


Figure 7—Evaporation Curves for Organic Solvents

fit these new substances. For example, ordinary untreated gum dammar is not entirely compatible with nitrocellulose when ethylene glycol monoethyl ether is the solvent employed. If, however, the gum dammar has previously been dissolved in alcohol, the slight waxy and insoluble residue rejected, and the gum recovered by evaporation of the alcohol, it is now found to be entirely compatible with the combination mentioned above and produces beautiful, clear, lustrous films.

The usual type of ester gum is not compatible with ethylene glycol monoethyl ether and nitrocellulose, but a mixture of ester gum and alcohol-soluble dammar prepared as above is entirely compatible if the ester gum content of the mixture is not more than 75 per cent. A small amount of phthalic anhydride-glycerol resin added to ester gum also makes the latter compatible.

Another and easier way of making gum dammar compatible with solutions of ethylene glycol monoethyl ether is as follows: The gum dammar is first dissolved in toluene. Twenty or thirty per cent of ethylene glycol monoethyl ether is added to this solution, as a result of which a precipitate will be produced. The waxy precipitate is filtered off. The filtrate may be used in nitrocellulose lacquers without further treatment and produces excellent films without the slightest suggestion of haze.

Since it is possible to modify these glycol derivatives by the addition or substitution of an alcohol, ether, ester or ketone group, it follows that it is also possible, within very wide limits, to produce a solvent that will comply with predetermined specifications embracing solvent properties with respect to nitrocellulose and gums, boiling point, rate of evaporation, resistance to water, and character of the finished film.

Although the experimental work is still somewhat incomplete, nevertheless, sufficient data have been secured over a period of several years to indicate that, without doubt, these glycol ethers will have an important place in the lacquer industry. One of them is already being produced in large quantities and used in the manufacture of a brush lacquer that can be as readily and simply applied as an ordinary varnish or paint.

Further development will undoubtedly extend the fields in which these compounds may be used and as the methods of production have been worked out for practically every compound discussed in this paper, their production in the future will be limited only by the requirements of the lacquer industry.

Acknowledgment

The author is indebted for much of the experimental data reported in this paper to F. W. Lommen, Herman Heckel, and Donald C. Lewis, who conducted the work for the Carbide and Carbon Chemicals Corporation under a fellowship arrangement at the Mellon Institute, Pittsburgh, Pa.

Special acknowledgment should be made to the Zapon Company who have cooperated in the preparation of glycol ether lacquers and on matters of practical lacquer application.

Safeguarding Laboratory Motors¹

By H. L. Trumbull

THE B. F. GOODRICH CO., AKRON, OHIO

NEED arose in the writer's laboratory for a stirring motor to operate near a volatile, flammable solvent. To prevent explosions from sparks in the motor, the principle of the Davy lamp was applied. The air holes at the brushes (eight in number) were covered with 50-mesh copper gauze, welded on. The motor was then run (free and under load) in explosive mixtures of air with natural gas, gasoline vapor, and benzene vapor. No explosions occurred, although the motor was sparking badly at the brushes. Under similar conditions the unprotected motor invariably detonated the mixtures.

It should be noted that this device gives no protection in the improbable event of a spark between shaft and bearings. Gleim² recommends that mine motors and other motors in explosive atmospheres should be totally encased in sheet metal instead of relying on gauze protection. The writer's experience, however, shows that gauze gives adequate protection for small laboratory motors used in experimental work.

¹ Received June 7, 1926.

² *Bur. Mines, Repts. Investigations* 2422 (December, 1922).