2. Nitrogen and sulfur do not interfere with the use of the method, but the bomb described is corroded when chlorine compounds are burned.

3. No practical method of using this method in analyzing micro samples of liquids boiling below 100° has been developed.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE EXPLOSIVES CHEMICAL LABORATORY, EXPLOSIVES SECTION, PITTSBURGH EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE PROPERTIES OF GLYCOL DIACETATE[1]

BY C. A. TAYLOR[2] AND WM. H. RINKENBACH[3]

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Until recently the prohibitive cost of glycol diacetate, $CH_3.COO.CH_2.CH_2.OOC.CH_3$, prevented its use as a solvent; but now it is prepared on a large scale with a high degree of purity and is finding extensive application in the arts. Having a high boiling point, high solvent power, low vapor pressure and being non-inflammable, it was thought possible that this compound might be of use in the purification and crystallization of explosives. With this in view, a study of its physical properties was made in the Explosives Chemical Laboratory of the Pittsburgh Experiment Station of the Bureau of Mines, at the suggestion of and on material procured by Dr. Charles E. Munroe of the National Research Council.

Properties

Pure glycol diacetate is a colorless, neutral, mobile liquid possessing a slight, characteristic, though unobjectionable, odor. It may be prepared (1) from ethylene dibromide or diiodide and silver acetate,[4] (2) from ethylene dibromide and anhydrous potassium acetate[5] at 150° to 200°, or (3) by boiling a mixture of 74 g. of ethylene dibromide, 80 g. of sodium acetate, and 200 g. of glacial acetic acid for 35 hours.[6] It is now prepared on a large scale from derivatives of the chlorination of natural gas.[7]

A quantity of commercial glycol diacetate[8] of high purity, boiling at 188° to 189.6° (739.2 mm.), was purified in the following way. The water that may have been present was removed by treatment with calcium chloride. The clear filtrate was kept from contact with moist air and fractionally distilled at about 125° and 85 mm. The middle (and largest) of three

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[1] Published by permission of the Director, U. S. Bureau of Mines.

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[4] Wurtz, *Ann. chim. phys.*, [3] **55**, 433 (1859).

[5] Demole, *Ann.*, **177**, 49 (1875).

[6] Seelig, Ger. pat. 41,507 (1887).

[7] Meyer, Ger. pat. 332,677 (1921). Rodebush, U. S. pat. 1,430,324 (1922).

[8] Supplied by courtesy of the Carbide and Carbon Chemicals Corp.

fractions, representing about 70% of the volume treated, was retained and used in this study.

Specific Gravity.—As determined by the Westphal balance this was found to be as follows.

TABLE I

SPECIFIC GRAVITY

Temp., °C.	2.6	5.0	10.0	15.0	20.0
d_{15}	1.123_9	1.121_0	1.114_8	1.109_7	1.104_0

When these results are plotted they form a straight line which, on extrapolation, gives a value of 1.1266 for 0° as compared with Wurtz's[4] value of 1.128.

Boiling Point.—This was found to be 190.2° (760 mm.). The method will be described under the heading of vapor pressure. Wurtz[4] reported 186° to 187° and Demole[5] gave a range of 185° to 188°, but neither specified the pressure at which the determination was made.

Melting Point.—The melting point was determined as follows. A special, unsilvered Dewar bulb[9] was used as a container for about 100 cc. of glycol diacetate which was agitated by hand with a wire stirrer, and the temperature read by means of a calibrated pentane thermometer. Cooling was effected by immersing the bulb in liquid oxygen or in the cold vapor above liquid oxygen. Although the rate of cooling was controlled and agitation of the liquid in the bulb was maintained during this period, great difficulty was experienced in bringing about crystallization. In almost all cases the liquid merely became more and more viscous although it was supercooled to as low a temperature as —125°, there being formed a clear, solid glass which fractured on further cooling. When true crystallization occasionally took place, a fine, snow-like solid was formed. The bulb was then removed from the liquid oxygen or cold vapor and allowed to absorb heat from the air while the contents were agitated. The point at which the solid dissolved while the temperature remained constant was taken as the melting point. Four such determinations gave values of —31 ± 1°.

This tendency to supercool results in an apparent difference between the melting and freezing points. Local supercooling is found in the case of glycol diacetate even during crystallization accompanied by agitation. Using the same apparatus and means of cooling employed for determining the melting point, two determinations of the freezing point were made. This was taken as the temperature at which the mixture remained constant for a time while the crystalline solid phase separated. The values —40 ± 1° so obtained were about 9° lower than the melting point. Bouchardat[10] has noted a similar tendency to supercool and an apparent freezing point lower than the melting point in the case of glycol itself.

[9] Taylor and Rinkenbach, THIS JOURNAL, **46**, 1504 (1924).

[10] Bouchardat, *Bull. soc. chim.*, **43**, 613 (1885).

Vapor Pressure.—The vapor pressure of glycol diacetate was studied by boiling the substance under various reduced pressures. The apparatus train included a 20-liter bottle to insure constant pressure. The manometer used was graduated to 0.5 mm. and read by means of a cross hair. The readings obtained on this and the barometer were reduced to pressures in millimeters of mercury at 0°. The determinations were run under seven different barometric pressures. The thermometers used were calibrated and, for the most part, used with total immersion in the vapor. In other cases, corrections for exposed stem were added.

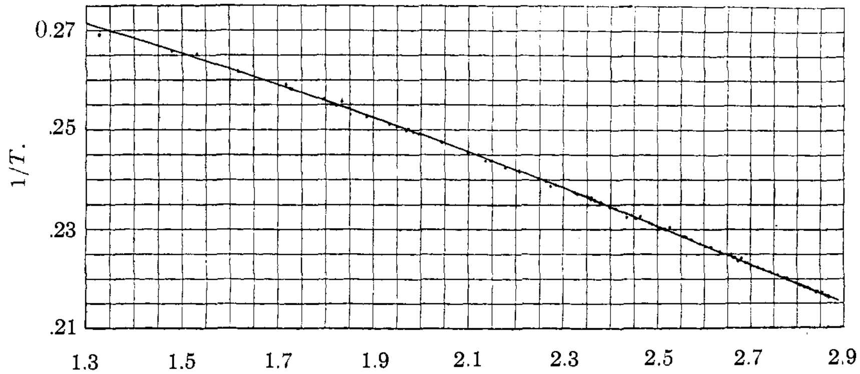

Fig. 1.

These results, when plotted as log p against $1/T$, give the practically straight line shown in Fig. 1. The maximum deviation from this was 12.3 mm., representing an error of 3.8%, but practically all of the points represented a deviation of less than 1% from the line. From this graph are obtained the following values for vapor pressures at regular temperature intervals.

Table II

Vapor Pressures of Glycol Diacetate at Regular Temperature Intervals

°C.	100.0	110.0	120.0	130.0	140.0
Mm.	26	44	70.0	107	158
°C.	150.0	160.0	170.0	180.0	190.0
Mm.	225	313	428	573	755

On extrapolation to 760 mm. pressure, this curve gives a value of 190.2° as the boiling point under standard conditions of temperature and pressure.

Determinations at pressures lower than 20 mm. could not be made because of the increasing tendency of the liquid to superheat, with consequent temperature fluctuations and bumping of the contents of the distilling flask. Extrapolation of the above curve to 25° indicates a vapor pressure of 0.2 ± 0.05 at that temperature.

Refractivity.—The refractive index of glycol diacetate was determined at a temperature of 20° with the monochromatic light of the sodium flame. The values found were: 1.4153, 1.4151, 1.4150, 1.4150, 1.4149, 1.4149; av., 1.4150. When this value is used in the formula $R_m = [(n^2-1)/(n^2+2)] \times (M/d)$, where R_m is the molecular diffraction, n the refractive index, M the molecular weight, and d the density at the same temperature (1.104), we obtain a value of 33.12 for R_m. It is of interest that, using the values for atomic refractions given by Roth and Eisenlohr,[11] we have

6 carbon atoms = 6 × 2.418 = 14.51
10 hydrogen atoms = 10 × 1.100 = 11.00
2 carbonyl oxygens = 2 × 2.211 = 4.42
2 ether oxygens = 2 × 1.643 = 3.29
33.22 calcd. mol. refractivity

Solubility and Solvent Power.—Glycol diacetate is rather soluble in water. Wurtz reports that at 22° it is soluble in seven times its own volume of water. It is completely miscible with ether, acetone, carbon disulfide, carbon tetrachloride, chloroform, methyl alcohol, ethyl alcohol, glacial acetic acid, benzene and dichloro-ethyl ether. It is not miscible with glycerol.

Careful determinations were made of the solubilities of explosive compounds in glycol diacetate at 25°. Two solutions of each substance, with an excess of solute present in each case, were fixed in a rotating wheel in a constant-temperature bath and maintained at 25.0° ± 0.05° for 36 hours. One solution was allowed to rise and the other to fall to 25°, thus approaching equilibrium from both directions. Samples were taken by means of a wagon pipet,[12] the solvent was evaporated by a stream of dry air and the solute weighed. The results obtained follow.

Compound	Trinitrotoluene	Picric acid	Trinitro-xylene	Trinitro-naphthalene	Tetranitro-aniline
G. of solute per 100 g. of solvent, av.	44.4	46.3	0.8	0.9	2.4

Because of the fact that it required about nine months to evaporate the foregoing samples, it was considered inexpedient to make determinations of a similar degree of accuracy on other and less important substances. Accordingly, the following approximate solubilities were determined at from 20° to 25° by shaking a weighed quantity of solute with a gradually increased amount of solvent until complete solution had been brought about. The results obtained are as follows.

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[11] Roth and Eisenlohr, "Refraktometrisches Hilfsbuch," Veit and Co., Leipzig, **1911**.

[12] Taylor and Rinkenbach, THIS JOURNAL, **45**, 44 (1923).

Compound	G. of solute per 100 g. of solvent
Trinitro-methylphenylnitramine (tetryl)	14
Trinitro-resorcinol	13
Hexamethylene-triperoxide-diamine, less than	0.9
Normal lead trinitro-resorcinolate, less than	.1
Cyanuric triazide, less than	.9

It was noted that when trinitrotoluene was dissolved in warm glycol diacetate and allowed to cool slowly to air temperature, extremely large and nearly white crystals were obtained, while the quick cooling of such a solution yielded small crystals. This is important when the control of the crystal size of explosive compounds is desired.

Summary

The most important physical properties of glycol diacetate have been studied and found to be such that its application as a solvent in the purification and crystallization of explosives may prove of value. It is neutral, stable, has a high boiling point and solvent power, is practically nonvolatile under ordinary conditions and will permit control of the crystal size of a solute.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE B. F. GOODRICH COMPANY]

RUBBER DI(HYDROXYPHENYL) AND ITS DIMETHYL ETHER[1]

BY HARRY L. FISHER, HAROLD GRAY AND EUGENE M. MCCOLM

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Twenty-five years ago C. O. Weber[2] showed that rubber "tetrabromide" and melted phenol react with the evolution of hydrogen bromide and the formation of a compound, $C_{34}H_{36}O_4$, in accordance with the following equation: $C_{10}H_{16}Br_4 + 4C_6H_5OH = C_{10}H_{16}(O.C_6H_5)_4 + 4HBr$. He considered it an ether, as indicated, and named it "tetroxyphenyl-polyprene." Other phenols reacted similarly, but thiophenol gave a different reaction, although hydrogen bromide was evolved, and phenol ethers like anisole did not react at all. The phenol product was found to form dark brown solutions in alcohol, acetone, ether, ethyl acetate and aqueous alkalies, and to be insoluble in benzene, chloroform, carbon disulfide, turpentine, and petroleum ether. Since the reaction was different with thiophenol and since there was no reaction with anisole, Weber concluded that "this is almost conclusive evidence that it is the hydroxyl hydrogen of the phenol which forms the point of attack in the reaction in question, and this fact is at the same time the reason why, in the above formula, the oxygen appears

[1] Presented in part under the title "The Tetra-hydroxyphenyl Derivative of Rubber and Its Tetra-methyl Ether," at the 62nd meeting of the American Chemical Society, New York, Sept. 6–10, 1921.

[2] Weber, *Ber.*, **33**, 791 (1900).