

IMMERSION LIQUIDS OF HIGH REFRACTIVE INDEX

C. D. WEST, *Harvard University*.

INTRODUCTION

For examination of materials under the polarizing microscope, and for other optical purposes, such as the measurement of refractivity of solids by the total reflection method, it is desirable to extend the range of immersion liquids as far as possible in both directions. The equation of state enters into the problem of finding liquids of extreme refractive index, whether high or low. Molecular refraction or polarizability runs parallel to the inter-molecular attractive forces. In consequence of this the high refractive index limit for the liquid state is set by the tendency of high index liquids to solidify under strong attractive forces—high internal pressure is the term sometimes used—just as they do under high external pressures. Conversely, the low index limit is set by the tendency of molecules, whose force fields are weak, to escape into the gas phase.

Attractive forces also vary with the strength of the molecular dipoles. The highest index liquids will be weakly polar if at all, for in this way the attractive forces are kept to the possible minimum. The lowest index liquids will be strongly polar, since such will be less volatile than non-polar liquids of the same refractive index. This advantage of polar substances in point of lower volatility is sometimes overlooked by mineralogists in making up sets of low index immersion liquids.

The prototype of high index liquids is yellow phosphorus—molecular weight 124, density 1.84, melting point 44° , refractive index 2.10. The tetratomic molecules of this element are dipole free, probably symmetrical tetrahedrons. The liquid, according to J. H. Hildebrand, is characterized thermodynamically by an extremely high internal pressure.

The prototype of low index liquids is hydrocyanic acid—molecular weight 27, density .702, boiling point 26° , refractive index 1.267. The molecules are linear and strongly polar. Other liquids of this class are water ($n=1.33$) and hydrofluoric acid (refractive index unknown). The condensed phase which will have the lowest refractive index is helium, whose intermolecular attractive forces are known to be the weakest of all substances; however, it can hardly be used as an immersion liquid under ordinary conditions.

By going to liquid systems of more than one component the rules of phase equilibria suggest possible gains at both ends of the liquid-refractive index scale.

SET OF HIGH INDEX LIQUIDS

The use of yellow phosphorus as a component of high index liquids has been suggested from time to time during the past seventy-five years.

Madan¹ pointed out the non-inflammable qualities of phosphorus-methylene iodide mixtures, and Borgström² described the use of phosphorus-sulfur mixtures with a third component, carbon disulfide or methylene iodide. The practical possibilities of such liquids have nevertheless received little attention from mineralogists.

We have found that a series of clear pale yellow liquids containing phosphorus-sulfur-methylene iodide, having the index range $n_D = 1.78 - 2.06$, is quite suitable for immersion purposes. The liquids are much less reactive than phosphorus alone, and with simple precautions may be used with confidence. They are reasonably constant in refractive index over a period of months when suitably stored. The sulfur depresses the solidification point below room temperature, the methylene iodide reduces the inflammability; although other substances could be used for the same purposes, the two named are preferred by reason of their high refractive index, low volatility and chemical stability.

Ternary System P-S-CH₂I₂. In making up high index liquids it would be desirable to have more information concerning solid-liquid phase equilibria in this ternary system, and in the corresponding one containing selenium. To date not even the binary systems have been examined in detail. Probably the P-CH₂I₂ and S-CH₂I₂ will be simple eutectics. The P-S system is remarkable not only for the ease with which the liquid phase may be supercooled, but also for the marked variation in properties with heat treatment. When these two components are mixed, without heating above 100° they are said to give a simple eutectic at 9.8° containing 22.8% S; but stronger heating brings about the formation of a series of solid sulfur-rich compounds with evolution of heat. The subject is reviewed by Mellor.³ It is expected that the ternary diagram for the unreacted system will have the appearance of Fig. 2.

The P-Se system has properties similar to those of P-S. It has recently been examined by Robinson and Scott.⁴ Borgström mentioned P-Se liquids with n_D up to 2.17, but these were dark and unstable in contrast to the P-S liquids.

Preparation. The 2.06 liquid is made by gently warming under water a mixture of yellow phosphorus (handle under water!), sulfur (can be obtained recrystallized from carbon disulfide), and methylene iodide in the approximate weight ratio of 8:1:1. Overheating is to be avoided. By mixing the 2.06 liquid with methylene iodide the graded series of liquids is made up, having compositions on the line drawn from point A in Fig. 2.

Optical Properties. The optical constants of the liquids were measured by minimum deviation through a hollow 50° prism.

A comparison of the present measurements with those of previous

writers⁵ is shown in Table 1 and Fig. 1. Dispersion $n_F - n_C$ increases from .038 to .065 as n increases from 1.74 to 2.06; the value .065 was also found by Damien for phosphorus. The temperature variation of n remains constant at .00065 per degree according to the accepted value for methylene iodide and the present value for the 1.99 liquid (range 6–27°).

TABLE 1. OPTICAL PROPERTIES OF HIGH INDEX LIQUIDS

	n	$n_F - n_C$	$-\Delta n/\Delta t$	Curve Fig. 1	Source
P (solid) 29°	2.15	.065	.00053	—	Damien, 1881
P (liquid) 44°	2.10	.063	.00116	I	
P-S-CH ₂ I ₂ 25°	2.06	.065	—	II	This work
	1.99	.058	.00065	III	
P-CH ₂ I ₂ satd. 18°	1.94	.055	—	IV	Madan, 1897
CH ₂ I ₂ 15°	1.74	.038	.00064	V	Timmermans, 1932

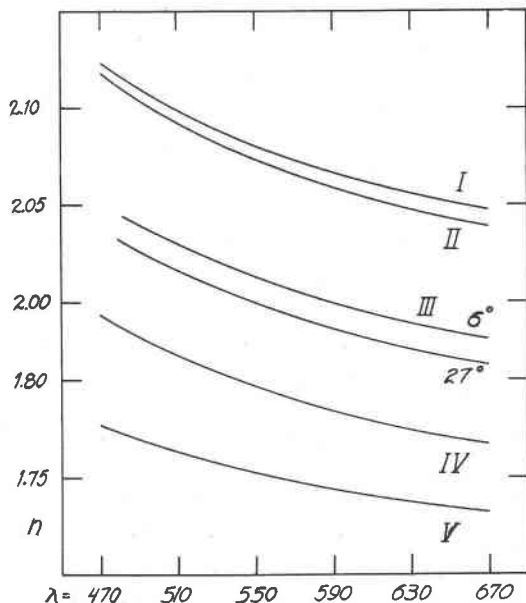


FIG. 1. Dispersion curves of high index liquids (see Table 1).

Damien reported a higher value for liquid phosphorus, namely .00116 per degree for the range 44–53°.

Storage, Stability. The phosphorus liquids are stored in glass stoppered bottles which are kept in a covered metal container; the latter to reduce fire hazard and to exclude light which has an adverse effect. In the present experiments a half inch layer of water was kept over the liquids, and

glycerine was also found to be satisfactory. Under these conditions the refractive index remains constant enough for practical purposes over at least five months, as shown by the following values of n_D corrected for temperature.

Initial Values	2.050	2.000	1.950	1.900	1.850	1.800
Three Months	2.050	2.001	1.948	1.897	1.850	1.802
6. 5 Months	2.050	2.000	1.949	1.898	1.850	1.801
9. 5 Months	2.049	2.000	1.950	1.898	1.851	1.802

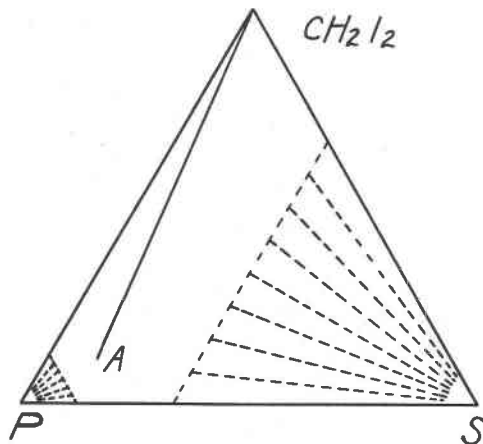


FIG. 2. System P-S- CH_2I_2 , 25° isotherm, schematic.

The stability of the liquids on storage without a water layer has not been determined, it could hardly be less than what is indicated by the foregoing. Under water the liquids slowly evolve H_2S gas, as shown by the smell. The 2.06 liquid at times deposits phosphorus crystals, but these redissolve with slight warming. If initially turbid the liquids tend to clarify themselves on standing, small amounts of solids settling to the water/liquid interface.

A few hours' exposure to direct sunlight spoils the liquids by inducing an irreversible reaction between phosphorus and methylene iodide with separation of solid products. The decomposition is hastened by the presence of water. The thermal reaction between these two substances is less marked, since they may be heated together under water for several hours at 80° with only slight resulting turbidity.

If left exposed on a compact surface like metal or glass the liquids do not take fire; but porous material like paper or cloth regularly takes fire after an interval, presumably due to volatilization of methylene iodide.

Method of Use. The liquids are transferred from bottle to object glass by means of a small pipette, the film of water is removed by touching

with a strip of filter paper, the latter is discarded under water. After immersion the solid is examined in the usual way under a cover slip. Used slides are discarded under water. Carbon disulfide may be used as a solvent for the liquids, with due caution since it is itself volatile and highly inflammable.

Advantages. Phosphorus is inexpensive and readily available. The liquids are suitable for optical examination of low melting or unstable materials with which immersion melts cannot be used, for example many artificial crystals. Also they are more convenient and more accurate to use than the melts. In comparison with arsenic bromide-arsenic sulfide-methylene iodide liquids, the phosphorus liquids are more stable and in at least some cases less reactive with solids under examination.

Organic compounds containing unsaturated ring systems usually have one or two principal refractive indices above 1.80, these indices corresponding to vibration directions in the plane of the ring. The phosphorus liquids have been found to facilitate the examination of such materials.

SUMMARY

This article describes a set of immersion liquids for the refractive index range $n_D = 1.78 - 2.06$, made up of the components phosphorus, sulfur and methylene iodide. From five months' experience with the liquids it is concluded that they are practically stable and safe to use with proper precautions.

ACKNOWLEDGMENT

A search for high index liquids was undertaken at the suggestion of Professor E. S. Larsen, and the experimental work was made possible through the hospitality of Professor Charles Palache and the coöperation of Mr. Harry Berman of the Department of Mineralogy, Harvard University. To these men the writer offers his best thanks.

REFERENCES

- ¹ Madan, H. G., *Jour. Roy. Microscop. Soc.*, vol. 273, 1897; *Proc. Chem. Soc.*, No. 193.
- ² Borgström, L. H., *Comm. géol. Finlande Bull.*, No. 87, p. 58, 1929.
- ³ Mellor, J. W., *Comprehensive Treatise on Inorganic Chemistry*, 8, p. 1047, 1928.
- ⁴ Robinson and Scott, *Zeit. Anorg. Allgem. Chem.*, vol. 210, p. 57, 1933.
- ⁵ Data of Madan and Damien, cited by Mellor, *loc. cit.*, p. 763. Originals not consulted.