IMMERSION LIQUIDS OF RELATIVELY STRONG DISPERSION IN THE LOW REFRACTIVE INDEX RANGE (1.46 TO 1.52)[1]

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ABSTRACT

A graduated set of stable refractive index liquids of low to intermediate index may be made of mixtures of ethyl cinnamate (*trans*), $C_6H_5CH:CHCO_2C_2H_5$, (n 1.558), with either glyceryl triacetate, $(CH_3CO_2)_3C_3H_5$ (n 1.429), or tributyl phosphate (n), $(C_4H_9O)_3PO$, (n 1.422). Such liquid mixtures have appreciably higher dispersion than the liquids of comparable index in the sets now commonly available and furnish the desired dispersion coloration for the very useful "dispersion staining" and "focal masking" techniques of index comparison and determination. In addition, triethyl phosphate, $(C_2H_5O)_3PO$, (n 1.405), is suitable as an end member where stability requirements are less stringent, and cinnamaldehyde, $C_6H_5CH:CHCHO$, (n 1.619), may be used as the high-index end member if precautions are taken to minimize oxidation.

In applying dispersion coloration techniques for refractive index determination it is desirable that the immersion liquid have an appreciably stronger dispersion than the solid it is to match. Such techniques have been described by Dodge (1948), Emmons and Gates (1948), Cherkasov (1957), Feklichev (1961) and Wilcox (1962), and related techniques aimed at distinction between minerals in granular mixtures have been described by Crossmon (1948), Schmidt and Heidermans (1958, 1959) and Radczewski (1961). Most of the commonly used immersion liquids of index above about 1.52 do have adequately strong dispersion, but liquids of lower index have dispersions progressively less different than the dispersions of corresponding solids, so that the color effects become less striking. In some applications this is not a disadvantage, since it may enhance the sensitivity of the determination. Yet for routine work it is helpful to be able to observe a succession of limpid dispersion colors over a fair range of index, say about 0.01. Several end members are suggested in this paper for making up graduated sets of immersion liquids having the desired strength of dispersion.

Buerger (1933) and Butler (1933) have discussed required properties of end members of a graduated set of immersion liquids. Few liquids fulfill all the requirements, and if strong dispersion is also desired, the number of suitable liquids is limited further. Lacking tabulations of compounds giving all the properties pertinent to this problem, the search for suitable end member liquids must in part be hit-or-miss, and one should not expect to find a pair that fits the many prerequisites exactly nor to be certain that all the possible candidates have been con-

sidered. Much useful information is given in the Merck Index (Stecher 1960).

For the high-index end member, several compounds are available. Two having moderate refractive index but extraordinarily high dispersion are ethyl cinnamate (*trans*) (n_F-$n_C = 0.0277$ at $n_D = 1.558$) and cinnamaldehyde (n_F-$n_C = 0.0414$ at $n_D = 1.619$). Ethyl cinnamate is relatively stable but cinnamaldehyde, like its sometimes used crude equivalent, "cinnamon oil," gradually oxidizes on exposure to air, decreasing

TABLE 1. PROPERTIES OF POSSIBLE END MEMBER LIQUIDS

Substance and Formula	Refractive n_D^{25}[1]	Dispersion $n_F - n_C$[1]	Temp. Coef. $\Delta n/°$ C.[1]	Boiling point ° C. (750 mm)[2]	Solb'y in 100 parts water[2]
Ethyl cinnamate (*trans*) $C_6H_5CH:CHCO_2C_2H_5$	1.558	0.027$_7$	0.0004$_8$	271	insolb.
Cinnamaldehyde $C_6H_5CH:CHCHO$	1.619	.041$_4$	.0005$_0$	246[3]	0.15
Tributyl phosphate (*n*) $(C_4H_9O)_3PO$	1.422	0.006$_5$	0.0003$_7$	289 w/decomp'n	0.6
Glyceryl triacetate $(CH_3CO_2)_3C_3H_5$	1.429	.007$_2$	0003$_9$	259	7.1
Triethyl phosphate $(C_2H_5O)_3PO$	1.405	.005$_6$	.0003$_9$	215	solb. w/decomp'n
Diethyl oxalate $(C_2H_5OOC)_2$	1.410	0.007$_7$	.0003$_8$	186	sl. solb. w/decomp'n

[1] Measured on samples of Eastman Organic Liquids, Distillation Products Industries, Rochester 3, N. Y.

[2] After Stecher (1960).

[3] Also given as 251° C. by Stecher (1960, p. 1527).

the index of refraction and finally precipitating crystals of cinnamic acid.

For the low-index end member of the series, there does not seem to be any suitable liquid of exceptionally high dispersion among the commercially available compounds. The approach of Crossmon (1959) has been adopted therefore; namely, to seek a compound of *very* low-index, whatever its strength of dispersion, to which may be added a high-index, very-high-dispersion liquid and thus obtain stable liquid mixtures in the intermediate index range possessing greater than usual strength of dispersion. Several possible end members are listed in Table 1, along with pertinent properties. The variation of dispersion of their mixtures

and of other commonly used sets of immersion liquids are shown on Fig. 1, for comparison with several representative solids.

For a calibrated set of immersion liquids it is important that the index of each liquid remain constant from month to month during intermittent use in the laboratory. Crossmon (1959) mixed triethyl phosphate with ethyl cinnamate to obtain mixtures of high dispersion and appropriate
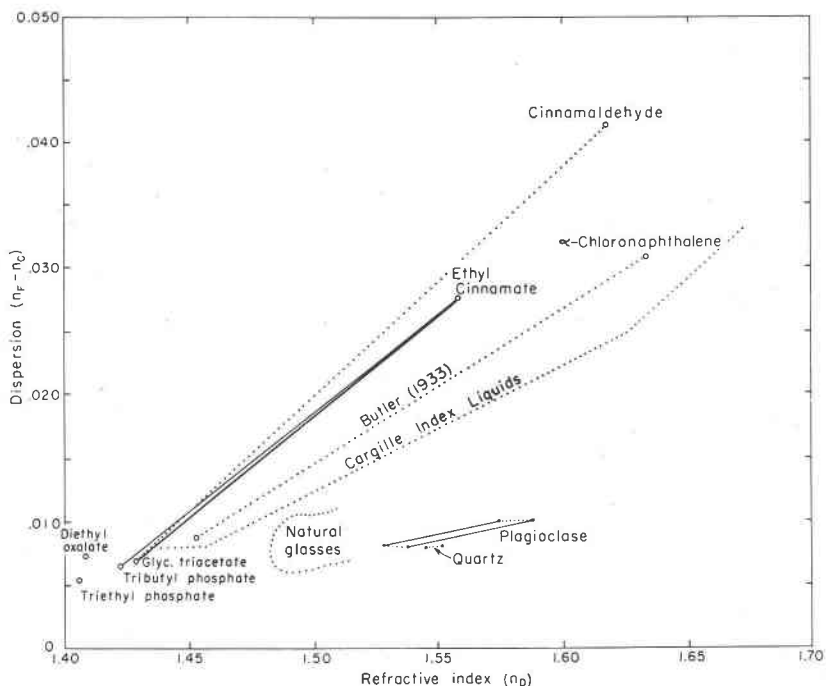

FIG. 1. Relations of dispersion and refractive index of some immersion liquids and typical solids.

refractive index for distinguishing one mineral from another in granular mixtures. Whereas the indices of these liquids do not change significantly during the time of observation in the mount, there is enough difference in the evaporation rates of their end members to require recalibration of the set of liquids at frequent intervals. Schmidt and Heidermans (1959) mixed diethyl oxalate $(C_2H_5OOC)_2$ with cinnamaldehyde, but Radczewski (1961) has pointed out that the indices of these mixtures cannot be depended upon to remain constant in a microscope mount unless an elaborate seal is made around the coverglass of each mount to

prevent differential evaporation. Judging from their boiling points (Table 1), the volatilities of both tributyl phosphate and glyceryl triacetate should be close to that of ethyl cinnamate or cinnamaldehyde, and these would therefore seem more promising candidates than the triethyl phosphate or diethyl oxalate.

To test the constancy of index of the various possible mixtures, sam-
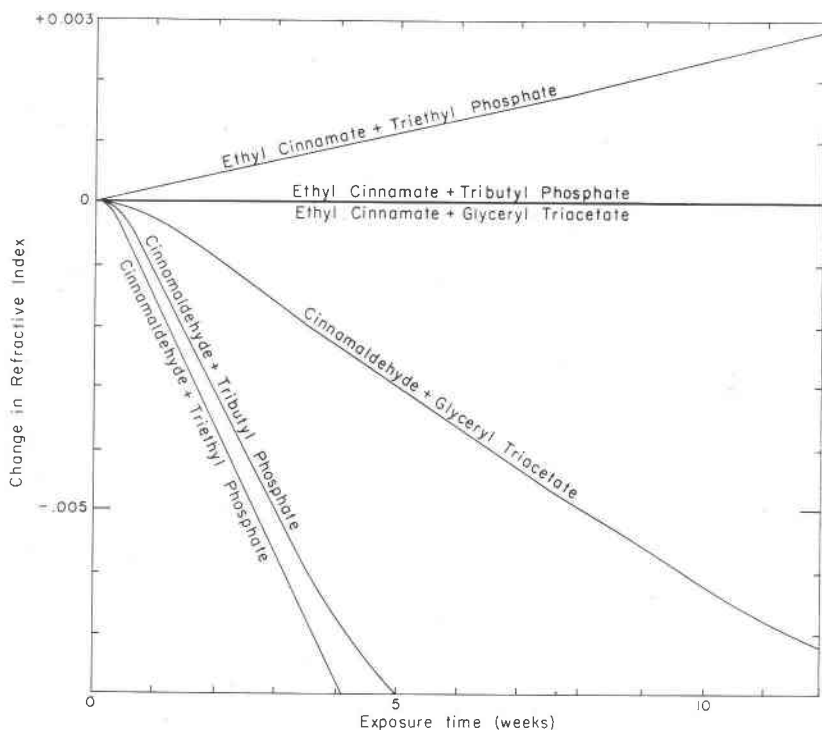

FIG. 2. Changes in refractive indices of 1-ml. samples of liquid mixtures of initial index near 1.50 during prolonged exposure to air and light.

ples of about 1 ml each were made up to index near 1.50. These were allowed to stand in their open vials in a lighted room, and the refractive index of each was remeasured at intervals over a period of 12 weeks. As shown graphically in Fig. 2, the mixtures of tributyl phosphate in ethyl cinnamate and of glyceryl triacetate in ethyl cinnamate did not change in index (within the $\pm .0003$ sensitivity of the measurements) even under these extremely unfavorable conditions. The mixture of triethyl phosphate with ethyl cinnamate gradually increased in index, as would be expected from their relative boiling temperatures. All mixtures

containing cinnamaldehyde decreased greatly in index, probably mainly as a result of the oxidation of the cinnamaldehyde.

For routine work either glyceryl triacetate or tributyl phosphate appear equally suitable as the low-index end member. For widest application, glyceryl triacetate is perhaps to be preferred, however, because of its lesser chance of chemical or solvent action on certain compounds that might be investigated or on adhesives used in special accessory devices on the microscope stage. These liquids have not been tested to establish that they do not give spurious results with montmorillonite-type minerals, as noted for some immersion liquids by Vendl (1945; *cf.* also Grim 1953, p. 286).

A set of liquids may be made up in volumetric proportions following the procedure of Buerger (1933, Fig. 1), making final adjustments as necessary for each bottle by adding small amounts of the appropriate end member to attain the exact index desired. For the work of this laboratory the sets have been made to cover the range 1.46 to 1.52 at intervals of .002. While it would be quite feasible to cover the entire range, 1.422 to 1.558, the mixtures of the lower part of the range do not have much better dispersion than the commonly available liquids (Fig. 1), and those of the upper part have dispersions greater than would generally be desirable for the focal masking technique.

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