

THE DOUBLE DISPERSION METHOD OF MINERAL DETERMINATION<sup>1</sup>

(PRELIMINARY PAPER)

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During the past two or three years the writer has conducted a series of experiments and collected data with the aim of improving the methods commonly used to determine minerals in the laboratory by means of the petrographic microscope. Attention was directed to two principal considerations. First, the index of minerals for light of the wave length of the sodium line can profitably be determined correctly to the third decimal place instead of within the limits expressed commonly by  $\pm .005$ . This greater accuracy is required by the greater detail with which minerals are becoming known and also by the realization of the importance of small variations in refractive index, especially with regard to their bearing on differences in chemical composition as brought out by the work of A. N. Winchell and others<sup>2</sup>. Second, it was hoped to increase the speed of an accurate study of the optical properties of a given mineral specimen. It is felt that some degree of success has been attained along both these lines, especially since even students with a preliminary training of two to four hours a week during one college semester, are able to determine the index  $N_D$  of the ordinary ray of quartz consistently with an error of  $\pm .0002$  and the entire determination requires fifteen minutes to half an hour, depending upon the student. It is felt, therefore, that others may be interested in the details of the procedure which are nearing completion as conceived by the writer. An early note was published<sup>3</sup> when it was first thought that temperature change and wave length change could both be used beneficially, but at that time neither this degree of accuracy was hoped for nor was it believed that the time required could be reduced to such an extent. It was thought at that time that the main benefit lay in being able to determine more than one index of a mineral grain of moderate

<sup>1</sup> The diagrams and subject matter of this paper have been given to Dr. A. N. Winchell for incorporation in the revised edition of his "Optical Mineralogy," Part I.

<sup>2</sup> A. N. Winchell, *Optical Mineralogy*, Part II, Numerous references to this subject in the literature are given throughout the text.

<sup>3</sup> A. N. Winchell and R. C. Emmons, *Some Methods for Determining Refractive Indices. Am. Mineral.*, Vol. 11, 1926, p. 115.

birefringence. Equal or greater emphasis is now placed on accuracy, speed, and the determination of the specific dispersion of minerals which is doubtless to receive progressively more attention in the future. The following notes and diagrams are offered in the hope that others may benefit by the information which they contain.

The methods of mineral determination commonly followed, employ the use of white light, which is to say light of all visible wave lengths ranging possibly from 4500Å to 7000Å. The sum total of white light is generally conceded to be equivalent to light of the wave length of the sodium flame, that is 5893Å. It is a common experience, in determining the refractive index of a properly oriented grain which should yield but one value, to observe two Becke lines or two illuminated sides of grains, according to the method employed. One of these lines or edges is blue and the other is yellowish red. They denote divergent indices. If such a grain be tested with light of one wave length (i. e. monochromatic light)<sup>4</sup> it will be found that for a particular wave length the grain disappears entirely, that is, yields no Becke line or illuminated edge, and for shorter wave lengths the grain is lower in index than the liquid, and for longer wave lengths the grain is higher in index than the liquid. The refractive index of a substance increases with decrease in the wave length of light being transmitted, and *vice versa*, the refractive index decreases with increase in the wave length of light. This property of substances is known as their chromatic dispersion and is a characteristic property. Further, it may be commonly observed that this increase or decrease in refractive index is less pronounced in the denser media, though this rule is by no means universal. But in general the dispersion of liquids is greater than that of solids, and though the dispersion of solids normally increases with their refractive index, the dispersion of liquids increases even more with refractive index. Further, amongst liquids there is a great difference in dispersive power. It is obvious then, that if a mineral grain is immersed in a liquid the refractive index of which is near that of the mineral, then by changing the wave length of light used, it should be possible, within certain limits, to change the index of the liquid to match that of the mineral. And the limits imposed by

<sup>4</sup> H. E. Merwin first used the dispersion of liquids in a practical way to determine  $N_D$  for minerals. M. Tsuboi elaborated his method, *Mineralogical Magazine*, Vol. XX, p. 108.

the liquid will be widened if the wave length dispersion of the liquid is high. To this end, therefore, a diligent search was made for liquids of high wave length dispersion, but in making the search detailed attention was paid to still another factor.

The refractive index of the liquid depends also upon the temperature of the liquid, decreasing with increase in temperature, and increasing with decrease in temperature. In fact, so important is this that modern refractometers are equipped with water circulation cells, the purpose of which is to maintain a controlled temperature for the liquid being measured. Although the thermal dispersion of liquids is comparatively high, yet that of minerals is, with very few exceptions, very low, being recorded in only the fifth or sixth place of decimals. There is available then, another means by which the index of a liquid may be changed to match that of a mineral grain within limits imposed by the thermal dispersion of the liquid.

By considering, then, in the search for new liquids, not only the wave length dispersion, but also the thermal dispersion, there was selected first, a set of 13 liquids, the index range of which extends from 1.40 to 1.78 without a single interruption, and usually with considerable overlap. This set covers a slightly greater range than the set of 60 liquids normally used and it enables the student to determine the refractive index to a correct figure instead of between the figures of two available liquids. Also, by eliminating the necessity of changing mounts so frequently, it reduces the required time for a determination very considerably.

In a great deal of work which the petrographer does the minerals on which interest centers are so commonly present in very small amounts that a grain once found should not be lost. Some petrographers recommend that a particular grain be transferred from one liquid to another but personally I have neither the ability nor patience required to do this, especially if the grain is small, and in any case I do not recommend it lest some of the first liquid adhere to the grain when it is immersed in the second liquid. It is, therefore, a keen satisfaction to the student to be able to work within a refractive index range on each mount instead of at a particular value. The increased accuracy which accrues from the use of this procedure is considerable as will be shown. And since the index of the immersion medium can be changed it is therefore possible, normally, after determining one index to rotate the grain

90° and to determine the other index. This becomes impossible for minerals of high birefringence, or if the higher index is at the lower end of the range of a chosen liquid and vice versa.

The most critical and most commonly recorded refractive index of minerals is that obtained for sodium light. But obviously it is seldom that the index of the liquid and that of the mineral coincide for light of this wave length. And since it is necessary to translate indices for light of other wave lengths into that for sodium, H. E. Merwin recommended that the index of the mineral should be determined for two or preferably three wave lengths by immersing the mineral successively in two or three liquids. If now the wave length of the light used is changed, causing a change in the refractive index of the liquid (and to a less extent of the mineral) and then the temperature of the mount is changed to bring about the opposite change in refractive index we have the mineral and liquid again matching in index. In other words we have accomplished all that we could have accomplished by transferring the particular grain being studied from one liquid to another, and by placing it in the exact orientation that it originally had. The actual procedure consists in changing the index of the liquid by a temperature change first and then changing the index back again by a change in the wave length. This is done because of the greater ease and speed of changing wave length. This may be done conveniently and rapidly as often as desired though three times at suitable intervals is sufficient. Three determinations suffice to give us the curve of dispersion of the mineral. Since the dispersion of minerals is not a straight line, two determinations are not enough for accurate work. By drawing the mineral curve, then, through the three points determined, the index of the mineral for sodium light may be read quite easily, or, for that matter, the index for light of any other wave length. A typical curve is shown in Figure 1.

The apparatus which the writer has employed in doing double dispersion work consists of a standard petrographic microscope on the stage of which fits a movable cell (Figure 2), through which water flows between two glass windows the lower one of which is thick, and the upper one of which is thin, to cut down insulation. The mount is made in the normal way upon the upper glass window. The path of light is from the lower nicol through the lower window, then through a thin layer of water, and through

the upper window and mount to the objective. Water of a controlled and variable temperature circulates through the cell thereby giving the desired control in temperature of the mount. The same water flows from the cell through an Abbe refracto-

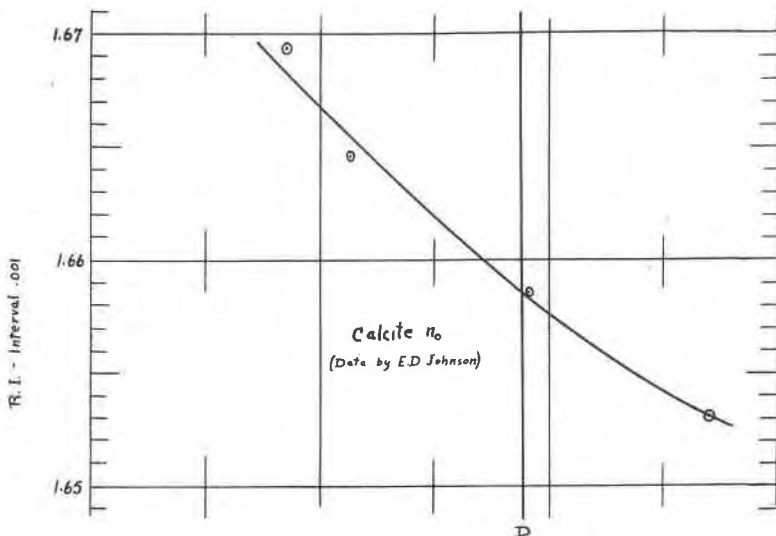


FIG. 1. Blank graphs of this type are kept in the laboratory.

meter on which is mounted the same liquid used in the mineral mount. A water heated and cooled cell is preferred to an electrically heated stage for these reasons: it gives an accurately



FIG. 2. Water circulation cell for the stage of the microscope.

identical temperature on the mount and the refractometer; it gives simplicity since the water circulation is required in any case for the refractometer; it gives more rapid and much lower cooling than an electric stage.

Two thermometers, which have been previously checked against each other are included in the system, one before the microscope cell, the other after the refractometer. When the thermometers agree within reasonable limits, then the index of the liquid on the microscope stage may be read directly on the refractometer at the same temperature. Next, the source of monochromatic light may be any standard monochromator having a constant deviation prism. The standard small Leitz monochromator illuminated by a Leitz Lilliput automatic arc has been found satisfactory. Bausch & Lomb makes a larger monochromator which is direct reading and gives more light. It is preferable to the Leitz, but costs slightly more. The Bausch & Lomb monochromator is being modified in minor details at the writer's request to make it more readily adaptable to microscope illumination for this purpose. The beam from a monochromator is focused on the mirror of the microscope, and this in turn adjusted in the ordinary way. When by proper manipulation an index of the mineral is made to coincide with that of a liquid, then the mirror of the microscope is tilted to project the monochromatic beam on to the mirror of the refractometer, and the refractometer is read, using the same wave length of light as was used on the mount. Abbe refractometers, however, do not read directly except for sodium light. A correction curve or tables<sup>5</sup> may be obtained from the manufacturers by which each reading may be modified by simple addition or subtraction giving the correct value. The attempt is being made to have the manufacturers modify an Abbe refractometer by adding a second fine adjustment, the purpose of which will be to correct the error introduced by the use of monochromatic light. The instrument should then read directly.

The procedure employed then may be summarized. First, the unknown may profitably be studied very briefly in the ordinary way using liquids of three or four indices if necessary in order to locate very roughly on the refractive index scale the mineral or minerals of particular interest. Then using the curves provided

<sup>5</sup> There is some question of the correctness of a curve to the fourth place of decimals. This does not affect the accuracy of the reading for sodium light as obtained from the plotted curve though it does to this extent affect the original readings for light of other wavelengths. The degree of possible error is greatest in the violet and at higher indices. It seldom affects more than the fourth place. It is not a consistent error.

in Figure 3 which show the "double dispersion" liquids on the refractive index scale, the proper liquid may be selected and a mount made. At the same time place a few drops of this liquid

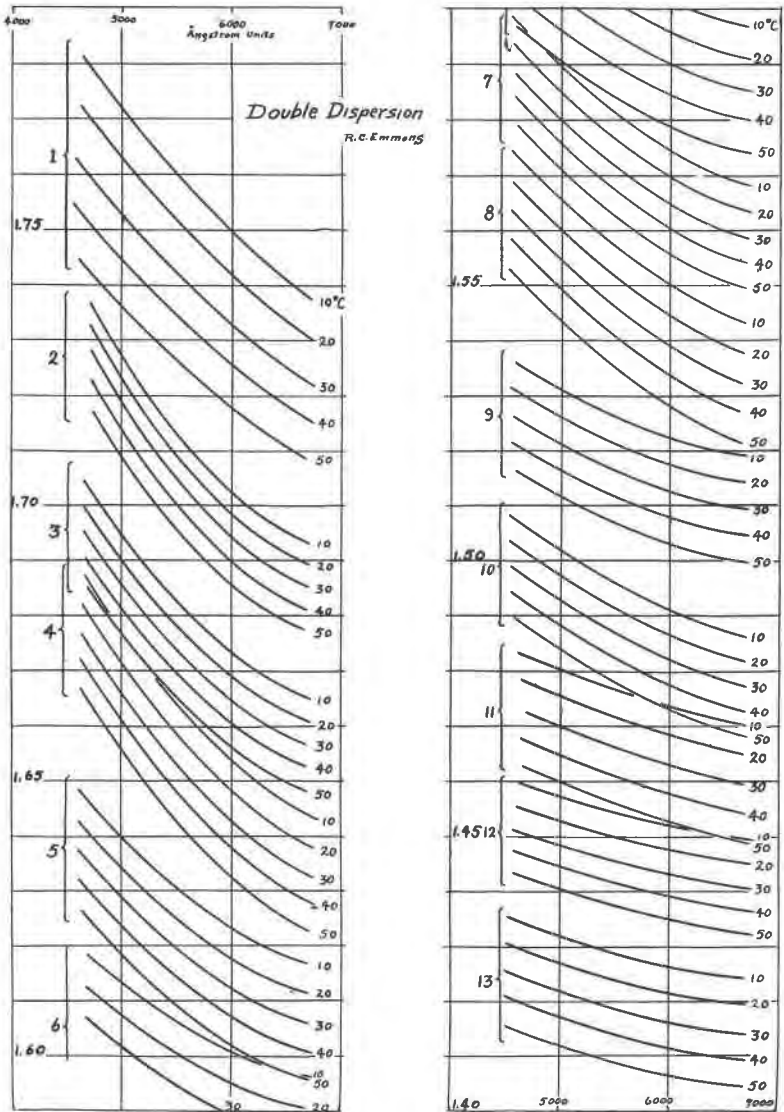


FIG. 3. Graphical representations of some of the optical properties of the liquids recommended for double dispersion use.

on the refractometer, turn on the water circulation, bringing the refractometer and the cell to the same temperature. Select a suitable grain and by adjusting the monochromator the index of this grain and that of the liquid can usually be made to agree. Read and record the temperature, the monochromator reading, and the refractometer reading, (making sure that the Amici dispersion prisms of the refractometer are set at 30 which is the neutral position proper for monochromatic light). Now change the temperature a few degrees, and adjust the monochromator to make the indices match again, and record the readings. Change the temperature once more and adjust as before. There are now available data for three correct refractive index readings on one ray. From the curve which these give the reading for light of the sodium wave length may be obtained. Also from this curve the dispersion  $N_p - N_c$  for this ray of the mineral may be read. If the first selected grain is an optic axis grain then the index is  $N_c$  or  $\beta$ . Next a grain of maximum birefringence may be selected and  $N_e$  determined or  $N_o$  and  $N_p$ .

In studying grains of very high birefringence it will be found necessary to use more than one liquid medium and so also if the mean index of the grain is near the limit of the range of the liquid being used. But this limitation is overcome to some extent by the fact that the liquids at their limits overlap considerably. In general practice it is recommended that the graphs of the liquids be kept in front of the student as it facilitates the selection of the liquid to be used.

The liquids listed are single compounds (not solutions) for the double dispersion set and mostly so for the single dispersion set. They cannot, therefore, change in physical constants and may be relied upon regardless of exposure or heating. Those which are mixtures are carefully selected on the basis of volatility. They must, however, be checked periodically. One mixture may be substituted in the double dispersion set to reduce cost as suggested in the table.

The first set of thirteen liquids the writer has termed the double dispersion set on the basis of the two types of dispersion employed in their use. One liquid, however, such as barium mercuric iodide solution, of high refractive index and high dispersion may profitably be included in the set, since it raises the available scale from 1.78 to 1.85, but it must be used with great caution as its



refractive index is dependent upon its concentration, and the concentration may vary with evaporation.

The second set of liquids the writer has termed the single dispersion set (Figure 4). It consists of 20 liquids most of which are

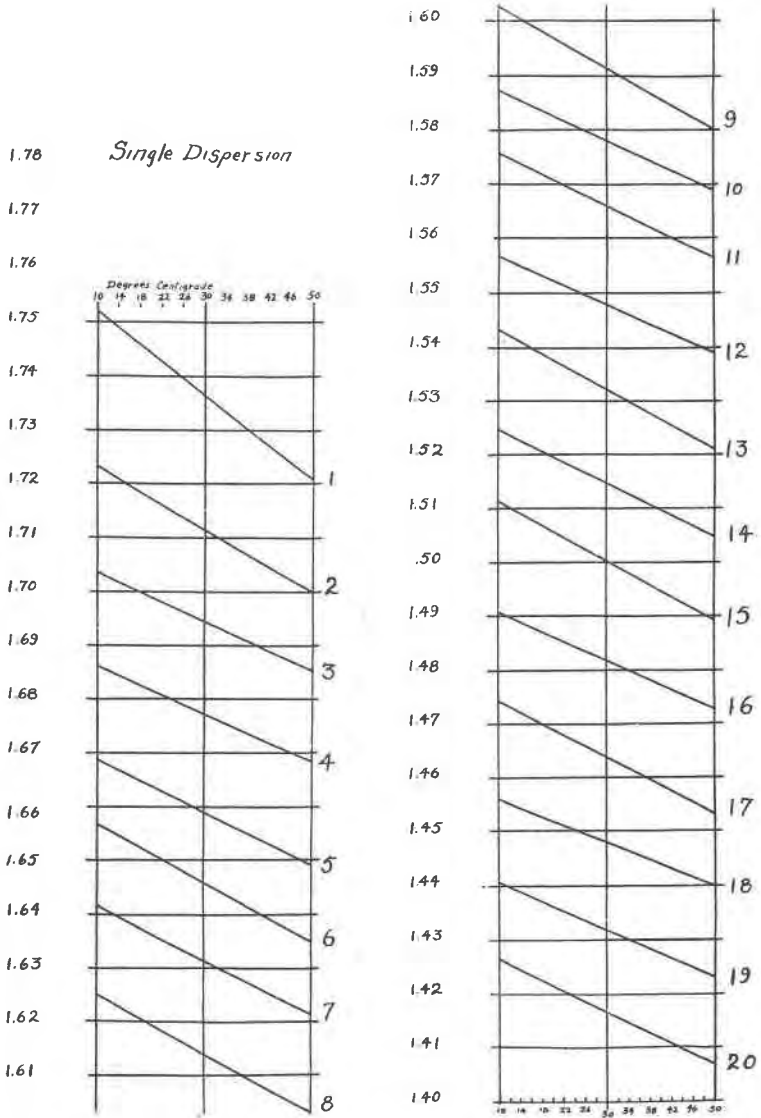


FIG. 4. Single dispersion liquids to be used for temperature change only.

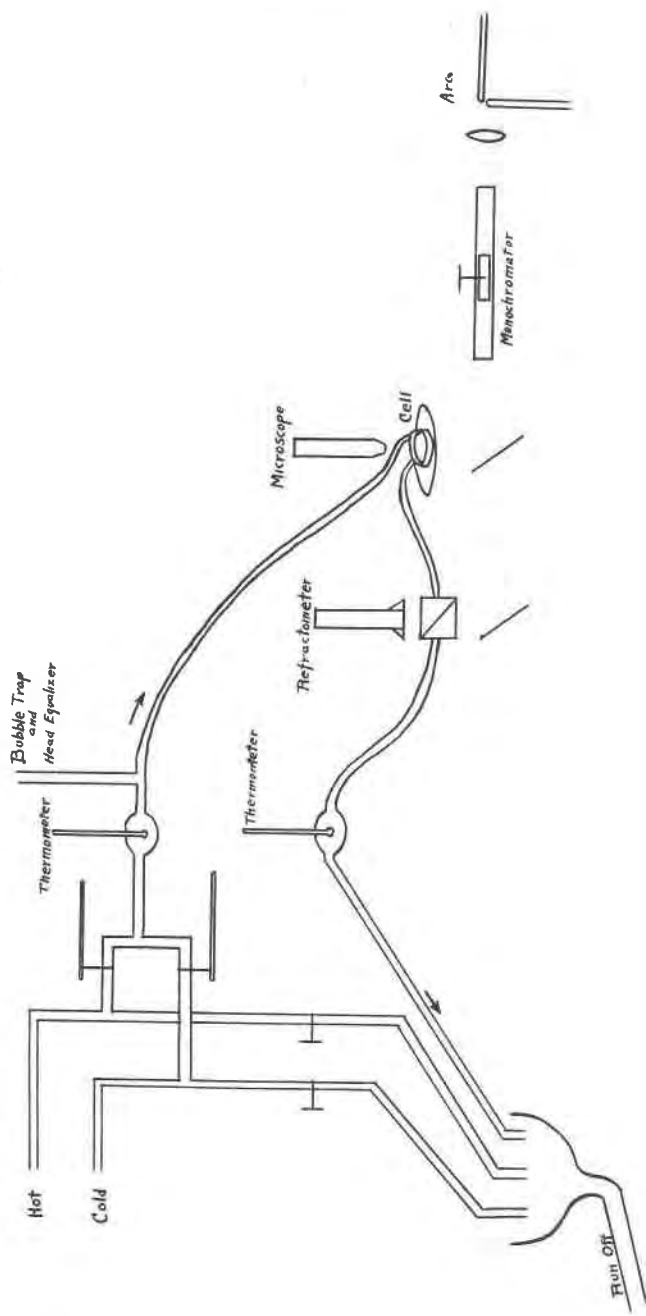


FIG. 5. General set-up of apparatus for double dispersion work. For single dispersion work a gas flame with sodium chloride in it is substituted for the monochromator and in the absence of a refractometer the curves of figure 4 may be used.

single compounds, but two are carefully selected mixtures, of approximately equal volatility used to fill gaps when suitable liquids of single composition could not be found. This set is intended for use in laboratories not equipped with a monochromator. The apparatus for temperature control may be built easily, and salts whose flames give standard wave lengths are always available. These liquids have high thermal dispersion.

In the selection and manipulation of these liquids, Dr. C. W. Muehlberger<sup>6</sup>, a qualified chemist, was untiring in his assistance. Without his advice the selection would not have been possible.

The general set-up of the apparatus is shown in Figure 5. The design of cell has been perfected by Mr. J. S. Hipple<sup>7</sup> who has made several models of different types in an attempt to get rid of the trapped air bubbles. The design now employed is quite good. Three cells are desirable in stock since the cover-glass windows are easily broken. These windows are cemented in by Canada balsam. The water valves used are standard main shut-off valves with the standard cones replaced by others having a narrow diamond shaped opening to give delicate control. These work very well indeed. In order to have hot and cold water at the control valves a constant overflow is maintained while working. All the work is conducted in a dark room.

Mr. W. B. Rayton of the optical division of the Bausch & Lomb Optical Co., has agreed to make all the parts necessary and the company will sell the entire set-up as a unit.

#### ACKNOWLEDGEMENTS

The writer wishes to acknowledge his indebtedness for advice and suggestions to Dr. C. W. Muehlberger and Dr. A. N. Winchell.

TABLE I. DOUBLE DISPERSION LIQUIDS

LIQUIDS	$N_D$
1. Methylene Iodide	1.742.....24°C
2. $\alpha$ -Iodonaphthalene	1.697.....27
3. $\alpha$ -Bromonaphthalene + Dibromonaphthalene	1.668 (variable)
3a O-Bromiodobenzene (to replace No. 3 and 4)	1.660.....28
4. Phenylisothiocyanate	1.646.....27
5. Iodobenzene	1.616.....27

<sup>6</sup> Dr. C. W. Muehlberger, Service Memorial Institute, Madison, Wisconsin, has kindly consented to make, purify and sell these liquids in sets until someone qualified can be found who is interested.

<sup>7</sup> Mr. J. S. Hipple, Service Memorial Institute, Madison, Wisconsin, has agreed to make these cells for general use.

6. Bromoform	1.592	.....	27
7. O-Toluidine	1.568	.....	27
8. O-Nitrotoluene	1.543	.....	27
9. Propylene Bromide	1.515	.....	27
10. Methyl furoate	1.484	.....	26
11. Methyl thiocyanate	1.467	.....	24
12. Trimethylene chloride	1.445	.....	26
13. Ethyl monochloroacetate	1.419	.....	26

Complete physical constants will be supplied in a later paper. The writer has given a tentative list of values more complete than this list to A. N. Winchell for publication in his Optical Mineralogy, Part I, Revised edition.

TABLE II. SINGLE DISPERSION LIQUIDS

LIQUIDS	<i>N<sub>D</sub></i>
1. Methylene iodide	1.742 ..... 24°C
2. Methylene iodide+Iodobenzene	1.715 (variable)
3. $\alpha$ -Iodonaphthalene	1.697 ..... 27
4. $\alpha$ -Iodonaphthalene+ $\alpha$ -Bromonaphthalene	1.6770 (variable)
5. O-Bromiodobenzene (or $\alpha$ -Bromonaphthalene+Dibromonaphthalene)	1.660 ..... 28 Do (variable)
6. Phenylisothiocyanate	1.646 ..... 27
7. S-Tetrabromoethane	1.6344 ..... 24
8. Iodobenzene	1.616 ..... 27
9. Bromoform	1.592 ..... 27
10. Anilin	1.581 ..... 24
11. O-Toluidine	1.568 ..... 27
12. O-Nitrobenzene	1.551 ..... 24
13. Ethylene Bromide	1.536 ..... 24
14. Propylene Bromide	1.515 ..... 27
15. Pentachloroethane	1.508 ..... 24
16. Methyl furoate	1.484 ..... 26
17. Methyl thiocyanate	1.4669 ..... 24
18. Isoamylsulphide	1.451 ..... 24
19. Ethyl dichloroacetate	1.4350 ..... 24
20. Ethyl monochloroacetate	1.4200 ..... 24

Since two (or three) of these liquids are mixtures they must be used with some degree of caution and checked periodically as are standard immersion liquids.

Liquid number 6 of Table I (number 9 of Table II) is a low boiling liquid with high volatility. It is hoped to be able to replace it when a suitable substitute is found. It is used here because of its very high thermal dispersion. At high temperatures it is necessary to add it periodically to the mount.

The iodides in the higher ranges of index are apt to become discolored by the liberation of iodine. The color may be removed quite well by adding an aqueous solution of sodium carbonate and shaking thoroughly. Dr. Muehlberger recommends this procedure.