

## IMMERSION LIQUIDS OF INTERMEDIATE REFRACTION (1.450-1.630)

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### ABSTRACT

A most convenient set of liquid standards for use in ordinary immersion technique has optical properties linearly related to index. This requires an optically ideal solution system. The series described here covers the intermediate index range (1.450-1.630) and has for end members  $\alpha$ -monochloronaphthalene and a high boiling kerosene fraction. The resulting solutions have index related to composition by practically a straight line, and temperature coefficients and dispersions are linear functions of index, hence the liquids constitute an optically ideal solution series. After eighteen months of laboratory use, the properties remain unchanged; the liquids are therefore excellent for ordinary immersion technique, and it is suggested that they might find use in the double variation method. Directions are given for the exact duplication of the series of liquids.

### INTRODUCTION

Lists of liquid standards for use in the determination of indices of crystals by the immersion method have been given by van der Kalk,<sup>1</sup> De Lorenzo and Riva,<sup>2</sup> Wright,<sup>3</sup> Merwin and Larsen,<sup>4</sup> Merwin,<sup>5</sup> Johannsen,<sup>6</sup> Larsen,<sup>7</sup> Borgström,<sup>8</sup> Emmons,<sup>9,10,11</sup> Chamot and

<sup>1</sup> Schroeder van der Kalk, Tabellen zur mikroskopischen Bestimmung der Mineralien nach ihrem Brechungsindex; 2 Aufl., *Wiesbaden*, 1906.

<sup>2</sup> De Lorenzo and Riva, Die Krater von Vivara auf den Phlegreischen Inseln: *Mem. Roy. Acc. Sci. Napoli*, **X**, 1901, pp. 1-60.

<sup>3</sup> Fred Eugene Wright, The methods of petrographic-microscope research: *Carnegie Publication*, No. 158, Washington, 1911, pp. 97-98.

<sup>4</sup> H. E. Merwin and E. S. Larsen, Mixtures of amorphous sulphur and selenium as immersion media for the determination of high refractive indices with the microscope: *Amer. Jour. Sci.*, **XXIV**, 1912, pp. 42-47.

<sup>5</sup> H. E. Merwin, Media of high refraction for refractive index determinations with the microscope; also a set of permanent standard media of lower refraction: *Jour. Washington Acad. Sci.*, **III**, 1913, pp. 35-40.

<sup>6</sup> Albert Johannsen, Manual of petrographic methods, *New York*, 1918, pp. 249-265.

<sup>7</sup> Esper S. Larsen, The microscopic determination of the nonopaque minerals: *U. S. Geol. Survey, Bull.* **679**, 1921, pp. 14-20.

<sup>8</sup> L. H. Borgström, Ein Beitrag zur Entwicklung der Immersionmethode: *Comm. Géol. de Finlande, Bull.* No. **87**, 2, 1929, pp. 58-63.

<sup>9</sup> R. C. Emmons, The double dispersion method of mineral determination (preliminary paper); *Am. Mineral.*, **13**, 1928, pp. 504-515.

<sup>10</sup> R. C. Emmons, The double variation method of refractive index determination (second paper): *Am. Mineral.*, **14**, 1929, pp. 414-426.

<sup>11</sup> R. C. Emmons, A set of thirty immersion media; *Am. Mineral.*, **14**, 1929, pp. 482-483.

Mason,<sup>12</sup> Winchell,<sup>13</sup> and Harrington and Buerger.<sup>14</sup> Earlier workers paid scant attention to properties other than index, but following the introduction of the Emmons variation methods,<sup>15</sup> the properties of temperature coefficient and dispersion have become of prime importance. Properties are listed rather completely for low index media by Harrington and Buerger,<sup>16</sup> for liquids of intermediate refraction by Emmons,<sup>17</sup> and for high index media by Borgström.<sup>18</sup>

Unfortunately, the liquids of the intermediate range listed by Emmons form a disconnected series, and consequently the properties of any one member may be *discontinuous* with respect to those of the adjacent members. The conveniences afforded by a series with optical properties *continuously* variable with refractive index have been stressed by Buerger in a preceding paper,<sup>19</sup> in which he suggests the use of optically ideal solutions which have properties linearly related to composition.

The common difficulty encountered with standards of liquid solutions is the comparatively rapid change in index with use due to differential evaporation of the end members. Johannsen prepared a set<sup>20</sup> which changed 0.003 in two years. Wright's standards<sup>21</sup> changed 0.002 in one year. It is not stated in which index region these maximum changes occurred, but a change of 0.004 in the quartz-feldspar index region was observed on an intermediate series (crude kerosene-halowax mixtures) used in this laboratory for three years. In the present paper, an optically ideal solution series is described in which the desired constancy has been attained.

#### DESIRED FEATURES OF AN IMMERSION SERIES

A complete set of immersion media consists of several series. For convenience, the components of the set used in this laboratory are

<sup>12</sup> E. M. Chamot and C. W. Mason, Handbook of chemical microscopy, Vol. 1, New York, 1930, pp. 378, 385.

<sup>13</sup> A. N. Winchell, The microscopic characters of artificial inorganic solid substances or artificial minerals, New York, 1931, pp. 61-70.

<sup>14</sup> V. F. Harrington and M. J. Buerger, Immersion liquids of low refraction: *Am. Mineral.* **16**, 1931, pp. 45-54.

<sup>15</sup> R. C. Emmons, Reference 9, pp. 504-515; Reference 10, pp. 414-426.

<sup>16</sup> V. F. Harrington and M. J. Buerger, *loc. cit.*, pp. 50-54.

<sup>17</sup> R. C. Emmons, Reference 11, p. 483.

<sup>18</sup> L. H. Borgström, *loc. cit.*, pp. 59-62.

<sup>19</sup> M. J. Buerger, The optical properties of ideal solution immersion liquids: *Am. Mineral.*, **18**, 1933, pp. 325-334.

<sup>20</sup> Albert Johannsen, *loc. cit.*, p. 262.

<sup>21</sup> Fred. Eugene Wright, *loc. cit.*, p. 97.

listed in Table I. Properties must be continuously variable with index within any given series, and should present as much continuity as possible from series to series. Both these requirements can be easily satisfied in the lower and intermediate ranges.

Considering a single series, the following features<sup>22</sup> are desirable:

1. Adjacent liquids should have closely identical optical properties other than index. Therefore, all the properties should be continuously related to composition and the increment other than index from member to member should be a minimum. This has been thoroughly discussed by Buerger.<sup>23</sup>

2. Any two liquids should be miscible, and the index of any intermediate member should be a straight line function of its composition. This feature allows one instantly and certainly to make up a liquid of any desired index from the available standards. The making of the original standards from the end members is similarly simplified.

3. The liquids should be permanent, which implies constancy of properties under all laboratory conditions.

TABLE I. TABULATED RANGES AND COMPONENTS OF AN IMMERSION SET.

	Range	Components
Solid-solid series	>1.850	Sulphur—Selenium melts and Piperine—Arsenic iodide—Antimony iodide melts
Solid-liquid series	1.850—1.785 1.780—1.740	Metallic iodides—Methylene iodide Sulphur—Methylene iodide
Liquid-liquid series	1.735—1.635 1.630—1.455 1.450—1.350	Methylene iodide— $\alpha$ -monochloronaphthalene $\alpha$ -monochloronaphthalene—Kerosene fraction Kerosene distillates*

\* Do not form a simple series according to the terminology adopted in this paper.

4. The extreme members of any series should have closely connecting properties to the adjacent member of the next series.

5. Solid matter should not separate out on standing.

6. They should be clear and colorless.

7. They should be free from objectionable odors.

<sup>22</sup> Esper S. Larsen, *loc. cit.*, p. 14.

<sup>23</sup> M. J. Buerger, *loc. cit.*

8. They should, preferably, be non-poisonous and harmless.
9. They should not dissolve inorganic material.

Any series should cover the maximum possible index range so that the variables in the complete set are at a minimum. Obviously, if three end members resulting in two series are utilized to cover a range which could well be covered by two end members and one series, an additional complication is introduced into the completed system.

#### SELECTION OF END MEMBERS

**GENERAL CONSIDERATIONS.** The first two requisites of the preceding section call for a series of liquids made up by mixing two miscible pure end members. Obviously, physico-chemical similarity between end members is desired. The third requirement stipulates that the liquids must have low vapor pressures at experimental temperatures, and that the vapor pressures of the end members be approximately equal, resulting in stability through minimum and equal evaporation of the end members. (This cannot be satisfied by the methylene iodide liquids, or liquids containing dissolved or suspended solid material.)

**THE LOWER END MEMBER.** Harrington and Buerger demonstrated that high boiling kerosene fractions have constant index values<sup>24</sup> with respect to evaporation, behaving essentially as pure liquids. As their distillates composed the individuals of the lower range, one of their higher members should constitute a favorable lower end member of the intermediate series.

Because of the nature of these hydrocarbons, any high boiling kerosene fraction is not a pure liquid but its optical properties are analogous to those possessed by a pure liquid.<sup>25</sup> The 220°–225°C fraction obtained by Harrington and Buerger<sup>26</sup> meets the requirements with a vapor pressure comparable to that of  $\alpha$ -monochlor-naphthalene (see beyond), a low index, and, as an end member, presents properties linking with those of the lower range.

Distillation of 3.5 gallons of kerosene was accomplished on a simple fractionating column without reflux control. 300°F flash-point kerosene is a higher grade raw material than crude kerosene and should be used. It is a cheap commercial product.

At temperatures greater than 200°C, fractions were isolated

<sup>24</sup> V. F. Harrington and M. J. Buerger, *loc. cit.*, pp. 50–51.

<sup>25</sup> V. F. Harrington and M. J. Buerger, *loc. cit.*, p. 46, footnote.

<sup>26</sup> V. F. Harrington and M. J. Buerger, *loc. cit.*, p. 50.

every 3° or 5°C depending on the volume of the fraction. The combination of cuts covering the 228°–240°C range was found to present the optimum qualities of index and volume. This combination of 1200 cc. volume was redistilled and sharper cuts taken. The fractions boiling off between 220° and 236° were combined and set aside as the lower end member which was a clear and virtually colorless liquid, possesses a faint paraffin odor and has an index value,  $n_D = 1.4500 \pm 0.0001$  at 22°C.

It is to be noted here that fractionating apparatus in general is quite individual, and in work with this type of liquid, where the separate cuts have distinct differences in refractive indices, the index of a cut is a better criterion than the temperature in considering the efficiency of the distillation. Hence, the index of each fraction should be tabulated to facilitate the combination of the optimum fractions as the end member.

**THE UPPER END MEMBER.** Mixtures of petroleum compounds and  $\alpha$ -monochloronaphthalene were known to be workable refractive standards.<sup>27</sup> Alpha-monochloronaphthalene was chosen as the upper end member partly because it was known to be completely miscible with kerosene, and partly because it gave a favorable combination of high index with high stability and freedom from color<sup>28</sup> and objectionable odor. Its boiling point is 260°C, and the particular stock utilized in this investigation has an index,  $n_D = 1.6324 \pm 0.0001$  at 22°C. Alpha-monochloronaphthalene is a commercial product and may be purchased at a reasonable cost from the Eastman Kodak Company of Rochester, New York.

#### MIXING THE END MEMBERS

The theory of liquid mixtures has been discussed by Buerger<sup>29</sup> with especial reference to the present case. It is convenient to know beforehand how the composition is related to the index, hence by mixing about five known proportions of the end members, shaking well, and determining their various indices, it is possible to predetermine this relation. The form of this relation is then plotted on graph paper, as in Fig. 1, with the dashed line at the center representing the straight line which would correspond to the mixing

<sup>27</sup> R. D. Reed, Heavy mineral investigations of sediments: *Econ. Geol.*, XIX, 1924, p. 332.

<sup>28</sup> Halowax is an impure variety of  $\alpha$ -monochloronaphthalene and separates gummy material which precipitates on the containers.

<sup>29</sup> M. J. Buerger, *loc. cit.*

curve if the system were absolutely ideal. However, the deviation of the curve from the theoretical straight line is very slight, and its only effect on the properties of the series is on the composition—index values. The upward arching probably indicates a slight increase in the additive density immediately following the mixing.

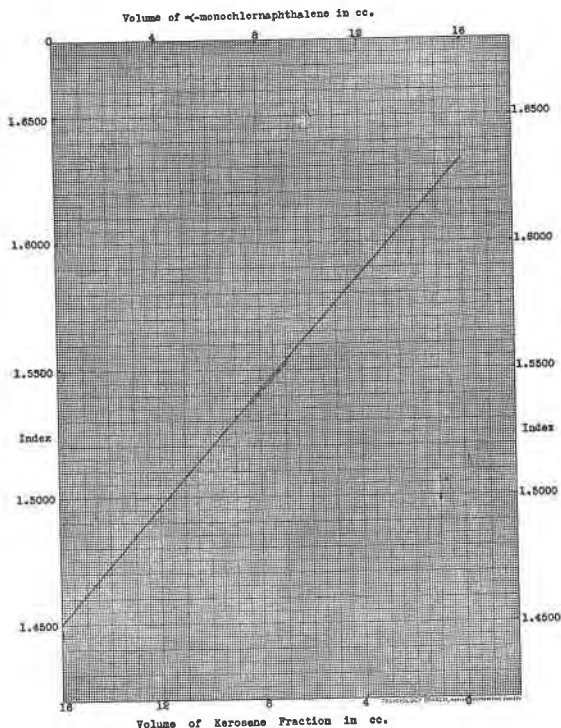


FIG. 1. Mixing curve which indicates the form of the composition—index relation for the series. The dashed line denotes the position of a straight line connecting the index values of the end members.

As the composition-index relation approaches a linear function and ideal conditions, the system may be termed near-ideal, and if other properties are linearly related to index, the system will be designated, optically ideal.

The actual working graph of Fig. 1 was plotted to a large scale, and the volumes of the end members to form any given index have been read directly. These volumes are listed in Table II.

TABLE II.

Kerosene fraction	Composition in cc.		Index, $n_D$ , at various Temperatures				Index, $n_D$ , at various Wavelengths				Dispersion† at 22°C	
	$\alpha$ -mono-chlorophthalene	$\beta$ -chlorophthalene	10°C	22°C	36°C	50°C	Hydrogen, # 4861A	Thallium 5351A	Sodium $n_D$ 5895A	Hydrogen % 6563A		Lithium 6708A
16.00	0.00			1.4500*			1.4567		1.4505			.0087
15.58	0.42		1.4598	1.4550	1.4498		1.4626	1.4583	1.4530	1.4480		.0093
15.13	0.87		1.4647	1.4601					1.4553		1.4523	.0099
14.70	1.30		1.4697	1.4650								.0105
14.28	1.72		1.4747	1.4700		1.4538						.0111
13.86	2.14		1.4798	1.4750	1.4693	1.4635		1.4752	1.4753	1.4720	1.4715	.0117
13.32	2.58		1.4849	1.4801		1.4692						.0123
12.99	3.01		1.4900	1.4852		1.4738						.0129
12.55	3.45		1.4949	1.4900		1.4786						.0135
12.11	3.89		1.4999	1.4950		1.4835						.0141
11.69	4.31		1.5047	1.5000	1.4940	1.4885		1.5049	1.5001	1.4959	1.4955	.0147
11.26	4.74		1.5097	1.5050		1.4931						.0153
10.82	5.18		1.5145	1.5100		1.4980						.0159
10.38	5.62		1.5199	1.5150		1.5040						.0165
9.95	6.05		1.5245	1.5201		1.5083						.0171
9.51	6.49		1.5295	1.5250	1.5191	1.5131		1.5313	1.5255	1.5203	1.5188	.0177
9.07	6.93		1.5345	1.5302		1.5181						.0183
8.63	7.37		1.5399	1.5350		1.5230						.0189
8.19	7.81		1.5446	1.5401		1.5282						.0195
7.75	8.25		1.5498	1.5451		1.5331						.0201
7.32	8.68		1.5549	1.5500	1.5440	1.5380		1.5566	1.5500	1.5446	1.5434	.0207
6.89	9.11		1.5597	1.5550		1.5430						.0213
6.46	9.54		1.5649	1.5600		1.5481						.0219
6.02	9.98		1.5699	1.5649		1.5530						.0225
5.58	10.42		1.5747	1.5700		1.5581						.0231
5.14	10.86		1.5797	1.5752	1.5690	1.5632		1.5826	1.5751	1.5687	1.5676	.0237
4.70	11.30			1.5800		1.5683						.0243
4.25	11.75			1.5851		1.5728						.0249
3.80	12.20			1.5900		1.5781						.0255
3.35	12.65			1.5950		1.5830						.0261
2.90	13.10			1.6000	1.5934	1.5879		1.6086	1.6000	1.5929	1.5914	.0267
2.45	13.55			1.6049		1.5928						.0273
2.00	14.00			1.6102		1.5975						.0279
1.55	14.45			1.6150		1.6025						.0285
1.10	14.90			1.6200		1.6076						.0291
0.65	15.35		1.6297	1.6250	1.6185	1.6126						.0297
0.20	15.80			1.6301	1.6239	1.6171		1.6398	1.6300	1.6218	1.6206	.0303
0.00	16.00			1.6324				1.6521	1.6326	1.6241		.0306
								1.6549				

\* Indices of the end members are correct to one in the fourth decimal place. Kerosene fraction = 1.4500  $\pm$  0.0001,  $\alpha$ -monochlorophthalene = 1.6324  $\pm$  0.0001

† Temperatures-coefficients computed from the formula locating the straight line in Fig. 4.

‡ Dispersions read from the straight line in Fig. 5.

## DESCRIPTION OF PROPERTIES

GENERAL DESCRIPTION. Following Buerger's reasoning,<sup>30</sup> the resulting system of mixtures should constitute optically ideal solutions if the end members were wisely chosen. The index should be a straight or near-straight line function of composition, and similarly, the other important properties should be linearly related to composition and therefore to index.

DETERMINATIVE METHODS. The optical properties of liquid standards are readily determined through index measurements subject to controlled variation of conditions. Thus, temperature coefficients are found by taking index readings at several temperatures and finding the change in index per degree temperature change, keeping the utilized wavelength constant; similarly, dispersions are found by index readings at a constant temperature and various wavelengths.

All measurements were accomplished under rigorous control of conditions. Indices for standardization and temperature coefficients were measured on a Spencer Abbé refractometer with two thermometers and three constant pressure reservoirs to insure accurate values of temperature. Indices were determined by the hollow prism, minimum deviation method, with a single circle goniometer, from a hydrogen source and lithium, sodium, and thallium flames. Temperature control of the liquid in the hollow prism can be maintained by circulating thermally controlled water through a hollow chamber which forms the base of the prism. Such a prism was designed by Professor Buerger, and experience has shown it to work satisfactorily. Fig. 2 is an explanatory diagram of the device.

INDEX. The indices of the end members were determined to fourth decimal place accuracy previous to plotting the mixing curve. The most convenient index of the members,  $n_D$  at 22°C, was measured following the mixing. Because of the lack of sensitivity of buret readings, the addition of a few drops of one of the end members was necessary in some cases to bring the liquid to the correct volume and consequently the desired index. The indices of the complete set at 22°C were remeasured two weeks after mixing to detect any possible changes. However, there were none beyond the limits of instrumental accuracy.

<sup>30</sup> M. J. Buerger, *loc. cit.*



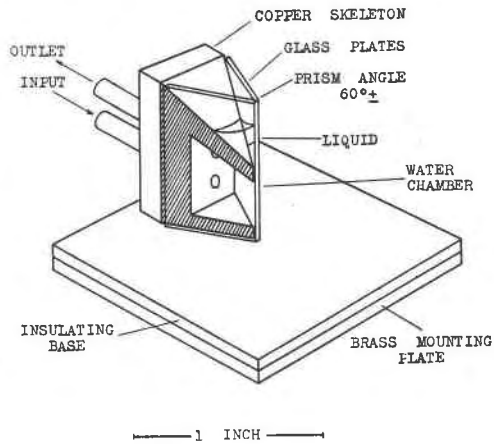


FIG. 2. Sketch of temperature-controlled hollow prism used in the minimum deviation method for index determinations. The glass plates are united to the copper element by Bakelite varnish.

Additional index values were measured at 10°, 36°, and 50°C. Indices are listed in Table II. The readings at 10° may be regarded as dubious as they were made in the summer, and fogging of the prisms (the dew-point phenomenon) caused imperfect resolution. The index of each member plotted against temperature is shown by the system of lines on the left-hand side of Fig. 3. Bearing in mind the unreliability of the 10°C readings, it can be seen that for any individual liquid the available data warrant a linear temperature-index relationship.

**TEMPERATURE COEFFICIENT.** The temperature coefficient,  $dn/dT$ , corresponding with the slopes of the straight lines in Fig. 3, is the rate of change of index with temperature. This property is utilized in the Emmons Variation Method<sup>31</sup> and must be accurately determined with a view to possible application.

The readings at 22°C and 50°C present the best experimental values with a maximum spread which covers most of the practical range of temperature variations. Therefore, temperature coefficients calculated over this range represent the best data. The temperature coefficients for this spread are shown plotted against index in Fig. 4. The scale of the temperature coefficients is greatly exaggerated; if it is plotted to the same scale as the index, the

<sup>31</sup> R. C. Emmons, Reference 10, pp. 418-420.

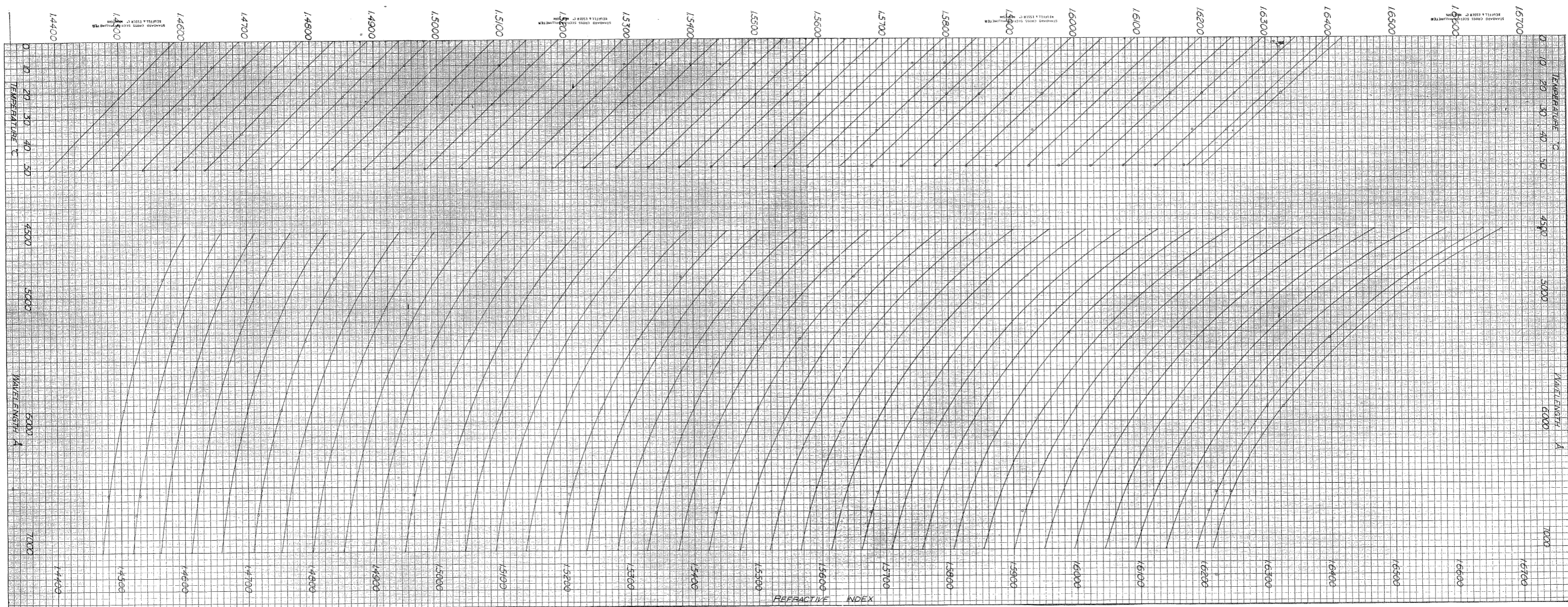


FIG. 3. Properties of the immersion series. The index of the members is plotted against temperature in the left-hand system of lines and against wavelength in the right-hand system of dispersion curves. Deviations from experimental points are explained in the text.

experimental points fall on a straight line, and the slope of the line is near zero.

The best straight line to represent the collection of experimental points was determined by the method of averages,<sup>32</sup> and its equation found to be:  $dn/dT = 0.0024332 n + 0.0000491$ .

The weighted and corrected temperature coefficients of the individual liquids have been calculated from this formula and listed

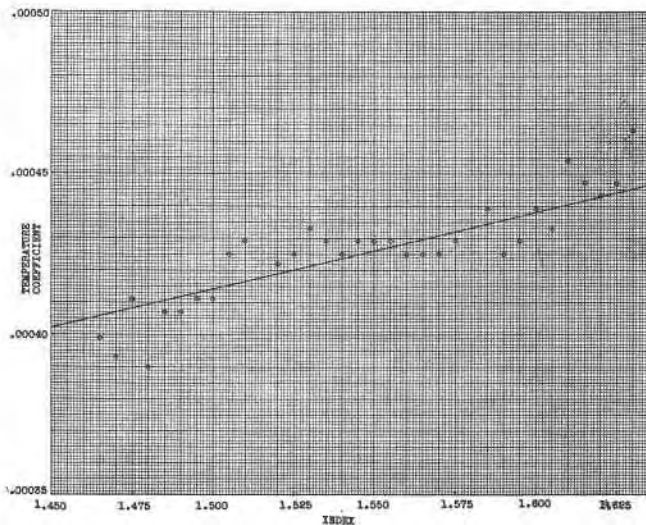


FIG. 4. Temperature coefficient,  $dn/dT$ , plotted against index,  $n_D$ , with the scale of the ordinate highly exaggerated. The best straight line representing the experimental points is given by:  $dn/dT = 0.0024332 n + 0.0000491$ .

in Table II. As these represent the best obtainable values, they have been used to determine the slopes of the temperature-index relations of Fig. 3, using the 22°C readings, whose certainties were most assured, to fix the positions of the lines. Any deviations of these lines from the experimental points is attributed to difficulties in temperature regulation.

DISPERSION. The arbitrary dispersion in common use,  $n_F - n_C$ , is the difference in index exhibited by a liquid between the *F* and *C* wavelengths of hydrogen. The variation methods utilize<sup>33</sup> dispersion in the general sense, i.e., the change of index with wavelength.

The indices of liquids spaced at  $n_D$  intervals of 0.025 (every fifth

<sup>32</sup> Joseph Lipka, Mechanical and graphical computation, *New York*, 1918, p. 126.

<sup>33</sup> R. C. Emmons, Reference 9, pp. 505-512; Reference 10, p. 417.

member of the series) were measured directly in the  $F$  and  $C$  wavelengths of hydrogen and in lithium, sodium, and thallium wavelengths. Results are tabulated in Table II. From these data,  $n_F - n_C$  has been computed, and is shown plotted against index in Fig. 5. The experimental values fell on a straight line whose equation is:  $(n_F - n_C) = 0.1200 n - 0.1653$ . Dispersion values for each individual of the series have been read from the graph and listed in Table II. Those for every fifth liquid coincide for the most part with the experimental values as these are exceptionally good.

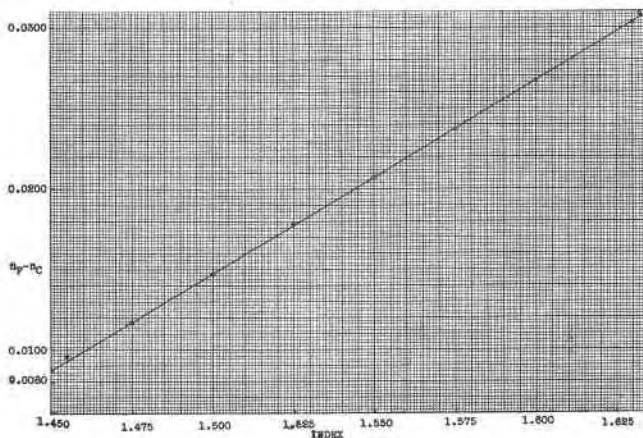


FIG. 5. Dispersion,  $(n_F - n_C)$ , plotted against index,  $n_D$ . The straight line connecting the points is given by:  $(n_F - n_C) = 0.1200 n - 0.1653$ .

The aforementioned prediction by Buerger that the dispersion of an ideal solution series will be linearly related to index is therefore fulfilled, and the liquids form an optically ideal system.

The dispersion curves of the individual liquids have been established so values might be read directly when using the variation method. This was accomplished as directed by Buerger<sup>34</sup> through the plotting of carefully determined wavelength-index values of a single liquid on Hartmann dispersion formula graph paper, reading off interpolated and extrapolated relationships, and drawing a progressive wavelength scale on a separate graph. Fig. 6 shows the system of straight line dispersion relationships for liquids spaced at  $n_D$  intervals of 0.025 as a result of plotting their values on this graph paper.

<sup>34</sup> M. J. Buerger, *loc. cit.*

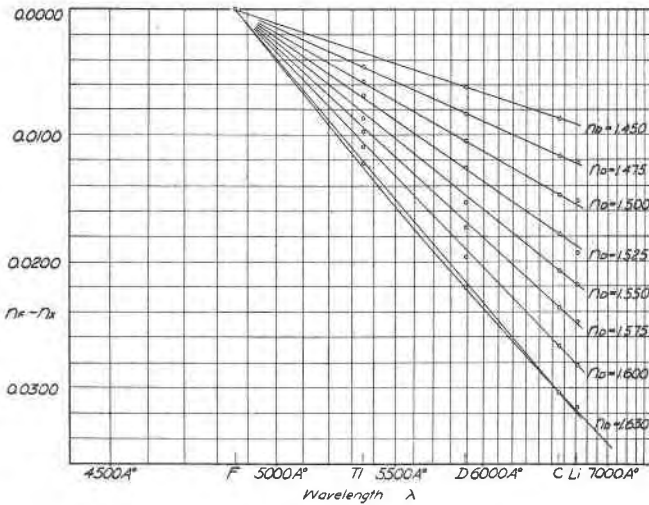


FIG. 6. Dispersions of liquids spaced at  $n_D$  intervals of 0.025, plotted on Hartmann dispersion formula graph paper. The lowest line represents the experimental points better than the corresponding straight line and is used in determining the wavelength scale of Fig. 7.

The above wavelength calibration is effected by reading values, not from one of the straight lines, but from a flat curve similar to the bottom line in Fig. 6, which represents the data somewhat better than the corresponding straight line. This gives index differences,  $n_F - n_x$ , which may be changed to absolute index, or which may give absolute index values directly, depending on the ordinate scale chosen. This holds for any wavelength or wavelength difference.

From the flat curve, differences in index of the liquid for differences of wavelength from the sodium wavelength ( $n_x - n_D$ ) were read. These were plotted vertically against the horizontal line,  $n_D n_D$ , of Fig. 7, resulting in the wavelength scale for this particular liquid. The upper straight line of Fig. 6 (the lowest liquid) was treated identically, and from the combination of points, straight lines were drawn which intersected at the 'projection point.' These lines are lines of equal wavelength. The height of a line, at any point, drawn to the 'projection point' from a designated value on the wavelength scale will represent the difference in index ( $n_x - n_D$ ) between this wavelength and the sodium wavelength at 22°C at that point. Buerger has stated that in optically ideal solu-

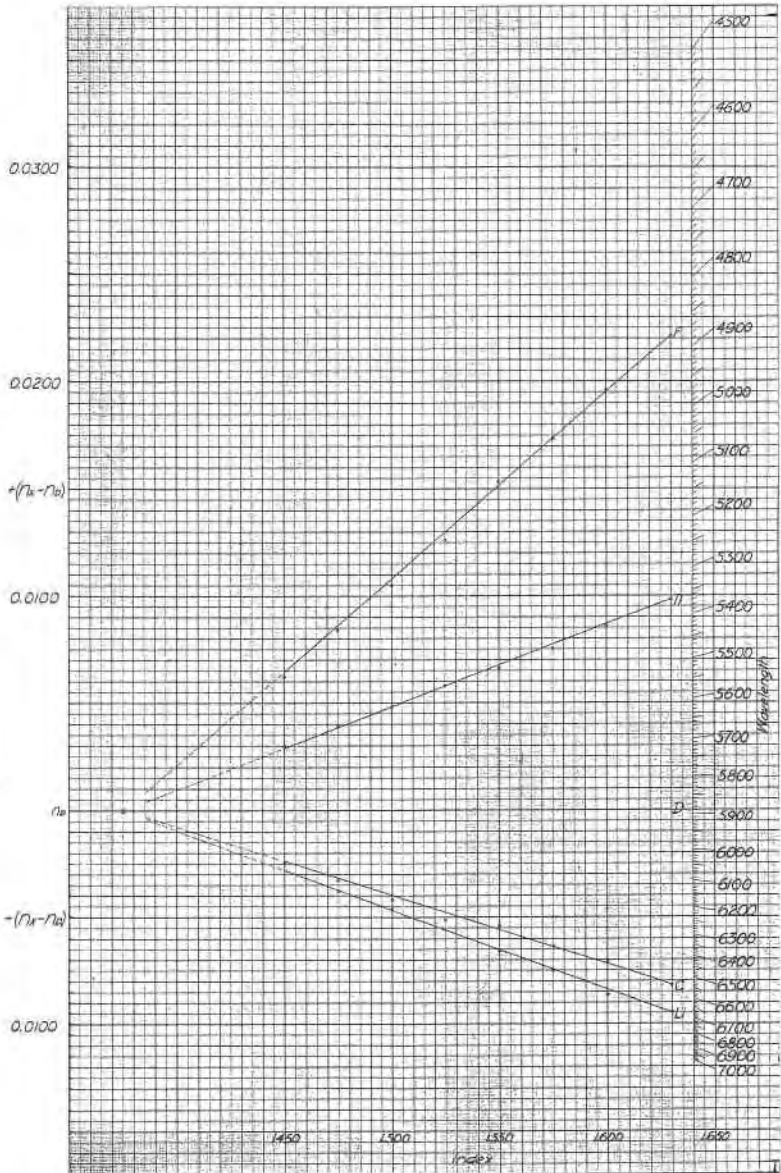


FIG. 7. Dispersion relations. Given a liquid whose index is known at 22°C for the sodium wavelength, to obtain its index at any other wavelength (i.e. given  $n_D$ , to find  $n_x$ ): locate the desired wavelength on the righthand vertical scale; draw a straight line from this point to the projection point; the vertical distance between this straight line and the base line at the given  $n_D$  value is the index correction to be algebraically added to  $n_D$  to get the desired index,  $n_x$ .

tion systems, such a proportionality relation between wavelength and index will necessarily have to hold true.

With this wavelength scale established, the accurate drawing of the individual dispersion curves on ordinary coordinate paper (as in Fig. 3) is simplified as an infinite number of points are available for any liquid of index  $n_D$ . Considering a single liquid, the index value in sodium light fixed, differences in indices for other wavelengths ( $n_x - n_D$ ) are read from Fig. 7, adjusted to absolute index  $n_x$ , and plotted against the wavelength. The system of dispersion curves on the right side of Fig. 3 shows the form of the index-wavelength relationship for the complete series.

CONSTANCY. The constancy of the properties of a series of immersion media depend on stability with respect to original composition. As the index is a direct function of composition, changes in index will denote inconstancy.

The primary fault of mixtures of liquids is the difference in vapor pressures of the components, hence, differential evaporation is to be expected with a resulting change in properties. Of these changes, index alone is serious; dispersion is a difference in index and would not change notably, and the change in the temperature coefficients would be in the fifth or sixth decimal places.

The end members and certain mixtures underwent evaporation

TABLE III. EVAPORATION RESULTS.

Liquid	Original Index	Index after 20 hours of evaporation	Change in Index
Crude kerosene	1.4483	1.4517	0.0034
300° F Flashpoint Kerosene	1.4558	1.4562	0.0004
Kerosene fraction end member	1.4500	1.4499	-0.0001
75% Kerosene fraction, 25% $\alpha$ -monochlornaphthalene	1.4997	1.5014	0.0017
50% Kerosene fraction, 50% $\alpha$ -monochlornaphthalene	1.5498	1.5531	0.0033
25% Kerosene fraction, 75% $\alpha$ -monochlornaphthalene	1.5872	1.5910	0.0038
$\alpha$ -monochlornaphthalene end member	1.6324	1.6323	-0.0001
Halowax	1.6345	1.6344	-0.0001

in the open air for twenty hours from 100 mm. diameter crystallizing dishes containing 10 cc. of liquid. Results noted in Table III, show that the end members are stable, and that 300°F flashpoint kerosene is a higher grade raw material than crude kerosene. The changes in index of the mixtures of the end members are ascribed to differential evaporation, but even these are not as serious as appears. Divided by twenty, the index change in one hour would be about 0.0002 if the surface is freely exposed, but in working with a covered slide, the amount of liquid surface is so slight that it is doubtful if any index change could be detected even if the slide were several hours old. However, elevated temperatures will decrease the time limit.

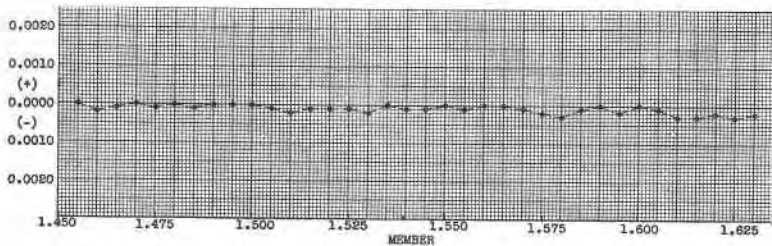


FIG. 8. Stability of the members of the series determined after 12 months use. The horizontal line represents the standardized indices and the encircled points show the deviation. The greatest is 0.0003 and the average is 0.0001.

The members of the series have been kept in the standard double-stoppered bottles, and the maximum index change after one year of laboratory use was 0.0003, the average being 0.0001. Fig. 8 shows these changes plotted against the members. Several index determinations were made after eighteen months, and as no further changes were indicated, the liquids fulfill the desired feature of constancy.

It should be noted that the liquids are constant with respect to both storage and use, and hence recommend themselves not only to ordinary comparative immersion methods, but also to possible application with the variation technique.

#### DUPLICATION

This series of immersion liquids can be duplicated exactly. This confers an advantage to those who do not have the time to analyze



optical properties in detail, as duplication of the series means duplication of the properties.

The duplication of the indices of the end members present the only difficulties, but this may be remedied by adjusting to the writer's mixing curve (Fig. 1), or by determining a new mixing curve.

Through close tabulation of distillate fractions, the index of the lower end member may be brought to the value,  $n_D = 1.4500$ , and will therefore correspond to a point on the present curve.

Should the index of the  $\alpha$ -monochloronaphthalene available be too high,  $n_D > 1.6324$ , a secondary standard of correct index may be formed by adding some of the lower end member, sufficient to bring it to this index, and this may be regarded as the equivalent of a primary standard.

Should the index of the  $\alpha$ -monochloronaphthalene, however, be too low,  $n_D < 1.6324$ , it cannot be raised without addition of material extraneous to the series. This difficulty may be overcome by a new mixing curve whose form is based on that in Fig. 1, but whose termination at 0.00 cc. kerosene fraction and 16.00 cc.  $\alpha$ -monochloronaphthalene is placed at the actual index value of the upper end member. To accomplish this, proceed as follows: On an exact duplicate of Fig. 1, locate the kerosene fraction index at 16.00 cc. kerosene and the  $\alpha$ -monochloronaphthalene index at 16.00 cc.  $\alpha$ -monochloronaphthalene. Connect these two points by a trial straight line. At a composition corresponding to 50% of each end member, locate an index 0.0010 higher than that indicated by the trial straight line. (Alternatively, this correction may be determined by measuring the index of a 50% mixture and subtracting the calculated value based on the straight line theory of liquid mixtures.) Now draw a smooth flat curve through the kerosene index point, the 50% corrected index point, and the  $\alpha$ -monochloronaphthalene index point. The resulting mixing curve will yield a system of liquids whose properties will be identical to those described.

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