[Contribution from the Severance Chemical Laboratory of Oberlin College.]

CHROMATIC EMULSIONS.

By Harry N. Holmes and Don H. Cameron.[1]

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Emulsions exhibiting a wide range of structural colors (suggestive of the chromatic scale of tones in music) were first prepared by Bodroux[2] who, however, neglected to use an emulsifying agent. Consequently his emulsions quickly separated into two layers. Our use of very different liquids with cellulose nitrate as an emulsifying agent enabled us to prepare remarkably beautiful emulsions that lasted for several weeks. We secured these colors in attempting to prepare a number of transparent emulsions.

Transparent Emulsions.—Ordinarily when two transparent liquids are emulsified a milky-white mixture results. For example, kerosene shaken with water gives such an emulsion. Yet transparent emulsions can readily be prepared. Transparency depends upon the relative indices of refraction of the two liquid phases. If both phases have the same refractive index, there will be neither reflection nor refraction and the system will appear homogeneous and entirely transparent.

Glycerol and olive oil are mutually insoluble and emulsify on shaking, forming a rather transparent emulsion. A more transparent mixture is obtained by dispersing glycerol in carbon tetrachloride using calcium oleate (previously dissolved in the carbon tetrachloride) as the emulsifying agent.

Glycerol and amyl acetate are mutually insoluble and yield an excellent creamy emulsion on shaking. The same is true of water and amyl acetate. Yet when a mixture of water and glycerol having the same index of refraction as amyl acetate was shaken with the latter liquid a perfectly transparent emulsion was obtained. Cellulose nitrate (11% nitrogen) was dissolved in the amyl acetate as emulsifying agent.

The refractive indices of these liquids as measured by an Abbe refractometer were as follows.

	n_4^{20}		n_4^{20}
Olive oil (commercial)	1.4690	Water	1.3330
Glycerol (U. S. P.)	1.4660	Glycerol-water	1.4028
Carbon tetrachloride	1.4600	Amyl acetate containing 6% of cellulose nitrate	1.4045

With the cellulose ester dissolved in amyl acetate the glycerol-water becomes the dispersed phase but with sodium oleate as the emulsifying agent dissolved in the water the phases are reversed—without loss of transparency.

[1] The authors are indebted to Mr. E. Wynne Boyden for valuable laboratory assistance in this research.

[2] Bodroux, *Compt. rend.*, **156**, 772 (1913).

Nujol (pure liquid paraffine) containing 2% of crepe rubber when shaken with an equal volume of glycerol yields a very good transparent emulsion. Here the rubber is the emulsifying agent and the glycerol the dispersed phase.

Pulverized cryolite is scarcely visible in water because its index of refraction is nearly the same as that of water.

Emulsions with Structural Colors.—In attempting to disperse glycerol in an acetone solution of cellulose nitrate we failed to get transparency. Since the index of refraction of the acetone (1.35886) was lower than that of the glycerol (1.4660) we added benzene (1.50144) cautiously to the milky emulsion in order to equalize the indices of the two liquid phases. Of course the benzene diluted the acetone thus becoming a part of the continuous phase. With cautious additions, and shaking, increased transparency was secured but accompanied by a startling development of colors. At first the emulsion became yellow as viewed from the side and a soft blue when held between the eye and the source of light. With further addition of benzene the yellow changed to beautiful pink while the blue became green. More benzene changed the pink to lavender and later to a peacock-blue. Finally, the emulsion lost color and became milky.

The colors were restored, in reverse order, by cautious additions of acetone.

The explanation of this phenomenon as given by Christiansen[3] and Bodroux[4] was verified by an examination of the Landolt-Börnstein tables of optical dispersive power of liquids. Benzene has more than twice the dispersive power of acetone. Optical dispersion is measured as the difference in the indices of refraction for light of two different wave lengths. In other words, a prism filled with benzene spreads light into a broader spectrum than does a prism filled with acetone. Consequently, drops of one liquid in another of very different optical dispersive power must give the effect of a great number of lenses or prisms with inevitable prismatic color effects.

Transparency is essential in chromatic emulsions for light of some color must pass directly through the emulsion. Yet transparency alone is not sufficient as shown by such emulsions as glycerol in carbon tetrachloride. Thus the selection of liquids for chromatic or structural color emulsions involves two factors: equality of indices of refraction and the

[3] Christiansen (*Wied. Ann.*, **23**, 289 (1884)) shook fragments of glass with a mixture of benzol and carbon disulfide. However, the work with emulsions affords a greater variety and far greater beauty than the work with irregular fragments of solids.

[4] Bodroux, Ref. 2, shook a saturated aqueous solution of sodium chloride with ethyl acetate and at a definite temperature found this transient emulsion transparent for light of a definite color. We secure our color change by carefully changing the proportions of the two miscible liquids in the continuous phase. Furthermore, our use of an emulsifying agent gives a definite stability to the emulsions.

greatest possible difference in optical dispersive power. From such values as those in the following table we were able to substitute other liquids for those first used—apparently a sufficient verification of the theory outlined.

I Dispersed phase	Index of refraction ° C	Optical dispersive power $(n_F - n_C)$ ° C
Glycerol	1.466 —20	0.007 —20
II Continuous phase		
(a) Acetone	1.35886—19.4	0.00684—19.4
Amyl acetate	1.40170—17.9	0.007 —17.9
(b) Carbon disulfide	1.61847—20	0.03210—20
Benzene	1.50144—20	0.01664—20
Toluene	1.4992 —18.7	0.0160 —14.7
Bromobenzene	1.55977—20	0.01923—20
Ethyl bromide	1.53806—20	0.01422—20
Benzyl acetate	1.50682—17.3	0.01660—17.3

Water may be substituted for glycerol, but the high viscosity of the latter adds to the stability of the emulsions and also to their beauty. It is interesting to invert a tube half filled with a chromatic emulsion and note that the intensity of color in the viscous film is practically as great as in the main body of liquid.

It is necessary to have two mutually soluble liquids for the continuous phase, one of them of high refractive index and high optical dispersive power. On careful addition of this liquid to a milky emulsion already prepared it is possible to change gradually both the refractive index and optical dispersive power. This insures the chromatic range of colors. Carbon disulfide is an excellent liquid to use (except for its offensive odor) because it stands high in both the essential physical properties. There is, however, considerable freedom of choice. The colors change somewhat with change in temperature since there is an unequal temperature effect on the optical dispersive power of the two phases. As Bodroux used only two liquids in each emulsion he was forced to secure his color effects by temperature change.

Cellulose nitrate (11% nitrogen) is an excellent emulsifying agent since it dissolves readily in acetone, amyl acetate and some other liquids, thus forcing the glycerol to become the dispersed phase, as desired. Raw crepe rubber may be substituted for the cellulose ester. For example, a 2% solution of rubber in toluene may be shaken with water which has been saturated with cane sugar to give it high optical dispersive power and high refractive index. Emulsions with a beautiful play of colors are secured. It is convenient to dissolve 20 g. of sugar in 1 g. of water somewhat above 20° and then cool. Slight inversion of the sugar with acid prevents crystallization. A trace of gasoline lowers the refractive index of toluene to a suitable point.

Potassium iodide gives water high optical dispersive power and a high index of refraction; so, Nujol may be dispersed in such a saturated solution using sodium oleate in water as the emulsifying agent. Prismatic colors are secured.

Resorcinol also gives water high optical dispersive power. A saturated solution is readily dispersed in a Nujol solution of rubber, developing good color.

For a beautiful lecture demonstration one may shake together 4 volumes of glycerol and 4 volumes of a 2 to 4% solution of cellulose nitrate in amyl acetate. To this 5 to 10 volumes of benzene are added, then more glycerol until rather viscous and finally more benzene in small additions, with shaking, until colors appear. The final emulsion may contain over 30% of glycerol. To view it best a 125cc. oil specimen bottle is used as container and held some distance from the source of light. A single source is best. The colors are exhibited in a cell with parallel sides but not quite so beautifully as in the bottle. On standing, these emulsions "cream" downwards but vigorous shaking restores much of their beauty. In many cases this cream becomes an emulsion gel due, probably, to a flattening of the drops of glycerol as they exceed 74% volume of the cream and to a coagulation of the cellulose nitrate in interfacial films.

If a sheet of white paper be held close to the emulsion but between it and the source of light the colors disappear only to reappear if a narrow slit be cut in the paper. The ordinary spectroscope with fairly wide slit does not produce a pure spectrum. That is, all the colors overlap somewhat. If they overlap still more, white light is produced in the center.

If we used only monochromatic light, there could be no optical dispersion.

Summary.

Two immiscible liquids can be emulsified, with suitable emulsifying agents such as cellulose nitrate, to produce (1) a transparent emulsion when (*a*) the refractive index of the two phases is the same, and (*b*) the dispersive power ($n_F - n_C$) of the two phases is the same; (2) a chromatic (structural color) emulsion when (*a*) the refractive index of both phases is the same, and (*b*) the dispersive power of one phase is much greater than that of the other. The greater this difference the more intense the resulting color.

OBERLIN, OHIO.