VIII.—*On some Organic Substances of High Refractivity, available for Mounting Specimens for Examination under the Microscope.*

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IN the course of experiments made with a view of obtaining some cement having the same index of refraction as Iceland spar for the ordinary ray (viz. 1.66), and therefore suitable for use in certain forms of polarising prism made of that material, I have had occasion to prepare, or procure, and examine several of the less known organic compounds of high refractivity. One or two of these do not seem as yet to have attracted the notice of microscopists, and I am induced to bring them before the Society, in the hope that they may be considered worth a trial by some who have had more experience than myself in the mounting and critical examination of specimens.

I must say at once that I have not yet been successful in finding an entirely satisfactory material; but I have thought it worth while to give a short account of what I have done up to the present time, in the hope of stimulating others in the search and of receiving suggestions for future experiments.

In the first place, let me state clearly and definitely what we want; the requirements of physicists and microscopists being in this matter pretty nearly identical. We want an irreproachably colloidal substance, with no tendency whatever to crystallise under any conditions, colourless, transparent, solid and tough at ordinary temperatures, but easily liquefied (or at any rate rendered viscous) by a gentle heat, stable under ordinary conditions of light and temperature, with no tendency to act upon or injure even delicate preparations, and—most important point of all—possessing a very high refractive power on light.

Perhaps we may consider Canada balsam (and one or two other similar gum resins) to have all the properties referred to except the last; and we may state our aim to be the discovery of a balsam-like substance, with a refractive index for rays of mean wave-length of not less than 1.66.

I do not propose to consider now any of the compounds of metals, such as arsenic tribromide, thallium chloride, mercury-potassium iodide, &c., which have been tried. Such substances, though useful for special purposes, and fulfilling excellently the requirement of high refractivity, have not the permanency and harmlessness which are desirable; they would quickly ruin, for instance, a polished surface of Iceland spar. I shall only draw attention to a few organic bodies

which seem to possess, in a greater or less degree, the qualities above mentioned.

1. *Meta-cinnamene*, or *meta-styrol* (formula of molecule, C_8H_8). This is a body obtained by Blyth and Hofmann in 1845,* from cinnamene, the essential oil prepared by distillation of styrax, a substance used occasionally as a mounting medium itself. When cinnamene is either (*a*) exposed to sunlight for three weeks, or (*b*) heated to $100^\circ C.$ for three days, or (*c*) heated in a sealed tube to $200^\circ C.$ for half an hour, it is converted, without change of chemical composition, into a polymeric form, a transparent, glass-like solid, viz. *meta-cinnamene*. The specimen I exhibit was prepared by the last-mentioned method, and retains the shape of the tube in which it was made. It is quite colourless and transparent, permanent under all ordinary conditions, and without the slightest tendency to crystallisation even after twelve years' keeping. It is remarkably tough, like horn, at ordinary temperatures, but is softened by a moderate heat, becoming flexible like gutta-percha, but not a viscous fluid like Canada balsam, except at a temperature slightly above $200^\circ C.$, at which it begins to volatilise and change back into the liquid form,—ordinary cinnamene. It shows no considerable adhesiveness to glass, and its coefficient of expansion differs so much from that of glass that a layer of it spread, while hot, upon a glass plate separates from it on cooling. In order to determine its refractivity, I constructed a small hollow prism of brass, open at the top, with sides of thin glass plates, and having a refracting angle of $51^\circ 7' 0''$. This was heated in an air-bath, and some *meta-cinnamene* was placed in it, the heat being raised until the body melted down into close contact with the sides of the prism. The angle of minimum deviation for several rays was then determined by a spectrometer, and the indices of refraction calculated by the usual formula. Thus the index of refraction for yellow sodium light (Fraunhofer's line D) was found to be 1.597 (at $15^\circ C.$). This is decidedly higher than that of most other resins; and although *meta-cinnamene* itself is hardly adapted for a cement or mounting material, it is likely to be very useful, from its toughness, transparency, and permanency, for giving body and strength to other cements, as I shall have occasion to notice further on.

2. *Quinidine* (formula of molecule, $C_{20}H_{24}N_2O_2$). This is one of the group of alkaloids occurring in cinchona bark, and is so essentially crystalloidal in character that I never thought of examining it until a few weeks ago, when my attention was kindly drawn to it by Mr. Lewis Wright and Mr. Nelson. I believe that it has pleased and plagued microscopists for several years, the conditions for ensuring its permanency in the colloidal form not having been satisfactorily made out.

As ordinarily obtained, quinidine is a hydrated salt (one molecule associated with two molecules of water), crystallising in colourless

* 'Memoirs of the Chemical Society,' ii. p. 334.

monoclinic prisms. The associated water of crystallisation is readily given off at temperatures between 120° and 130° C., and the crystals break up into a white powder, which, on being heated to a temperature of 170° C., melts into a nearly colourless liquid. At 200° C. the liquid begins to darken in colour, owing to incipient decomposition and liberation of carbon; hence in dealing with the substance as a "mountant" it is important not to raise the temperature more than necessary above the melting point. On cooling the liquid it solidifies into a light yellow resinous mass, having so slight a cohesion and so low a conductivity for heat that a block of it cracks up into small fragments under a slight stress or change of temperature, almost like unannealed glass; nor does very slow cooling appear to prevent this. I have also tried the effect of quick cooling by pouring liquid quinidine into cold water, but the only result seemed to be to make it more like a "Rupert's drop" than before.

When this resinous solid is again heated gradually, it changes into a mass of interlacing prismatic crystals and rosettes, forming a very beautiful polariscopic object. The change certainly begins below 90° C., but proceeds more rapidly at a few degrees higher. On further heating, the crystals melt, passing into the resinous colloidal condition mentioned above. I think it likely that the tendency to crystallisation complained of by those who have mounted objects in quinidine is mainly due to the slides having been exposed to a rather high temperature, such as that of a very hot room.

Also it should be noted that the presence of a few nuclei, such as particles of dust or of one or two minute unconverted crystals in the resin, would materially promote crystallisation. It would be advisable to filter the liquid, if practicable, before placing any upon the slide.

The fragility and unstable equilibrium of the colloidal form of quinidine caused me considerable difficulty in making a prism of it for the purpose of determining its refractivity. I was anxious, however, to do this, as the index of refraction was reported to be as high as 1.7 (for what wave-length I do not know). I am disappointed to find that the index for yellow sodium light is no higher than 1.602. Its coefficient of dispersion, moreover, is not particularly high; ($\mu_{ny} - \mu_{nr} =$) 0.043 (that of α -monobromonaphthalene between the same wave-lengths is 0.051).

From the above observations on the effect of heat on quinidine, it would seem advisable, in using the substance as a mounting material, to cool the slide pretty quickly, in order to get the resin past the turning point of 90° before it has time to take the wrong turn. But in this and similar substances there must, I fear, always remain the inherent tendency to revert to the crystalline condition, which is obviously the condition preferably assumed by the molecules when they are free to do as they like.

The parallel case of sulphur will occur to the mind of everyone. This substance takes three allotropic forms, two of them crystalline. When either of these latter forms is heated to 150°C ., it passes into a plastic colloidal condition, but can only be retained even temporarily in this form by being poured suddenly into cold water. In a few days it inevitably reverts to the crystalline condition; and the same change (as with quinidine) takes place quickly on heating the colloid to 100°C . Mr. Lewis Wright suggested to me that admixture with Canada balsam might prevent this; but on trial I do not find it answer.

3. *Naphthyl-phenyl-ketone* (formula of molecule, $\text{C}_{16}\text{H}_{12}\text{CO}$). This was discovered by Grucarevic and Merz,* and seemed at first likely to be an unexceptionable cement for polarising prisms. I prepared it by a method given in the paper referred to, which I need not describe here, as the details might not be intelligible without previous study of organic chemistry. It is a light yellow substance, viscous like Canada balsam at ordinary temperatures, but becoming more liquid when moderately heated, almost odourless, with little or no tendency to act on or injure other substances. The index of refraction for yellow sodium light I found to be 1.669 (at 15°), almost exactly that of Iceland spar for the "ordinary" ray. If there was no doubt as to its permanency, it would be very valuable for the purposes both of physical optics and of microscopy. The first specimen which I prepared remained for months quite unchanged (although tested by exposure to a temperature as low as -20°C .), but eventually turned into a mass of yellow crystals; and a fine polarising prism made for me in Paris on M. Bertrand's principle, in which this cement was used, after lasting for four or five years at least, has now become useless from the same cause. The ketone may be easily restored to the colloidal condition by re-distillation, but the change is not permanent. Hence, while I think the substance worth the attention of microscopists for temporarily mounting objects, my recommendation cannot extend further.

4. *α -monobromonaphthalene* (formula of molecule, $\text{C}_{10}\text{H}_7\text{Br}$), discovered by Laurent† in 1835. This substance is so well known to microscopists that I need not say much about it.

The index of refraction for sodium light is 1.66 (at 23°C .), and its dispersive power is almost exactly the same as that of carbon disulphide ($\mu_{\text{H}} - \mu_{\text{Na}} = 0.051$). It has a very high boiling point (285°C .), and is more stable than such bromo-compounds usually are. Hence it would be well adapted for filling hollow spectroscope-prisms but for its incurable yellow colour, which implies of course loss by absorption of the more refrangible part of the spectrum. It seemed possible that this yellow colour might be due to the presence of a trace of free bromine, and I have digested the liquid with zinc, sodium,

* 'Berichte der deutschen chemischen Gesellschaft,' vi. p. 1238.

† 'Annales de Chimie et de Physique,' lix. p. 216.

and mercury in the hope of removing this if present. I have also redistilled it under greatly reduced pressure (10^{-1} atmosphere), and filtered it through animal charcoal, but the yellow colour, though much reduced in intensity, still remains.

5. *Phenyl-thiocarbimide* (formula of molecule, C_6H_5CNS), a substance belonging to the class of mustard oils, one of the many discoveries of Dr. A. W. Hofmann.* I need not go into the details of its preparation, which are of more interest to chemists than to physicists, especially as I find that it can now be obtained commercially from Schuchardt, of Görlitz (English agents, Messrs. F. E. Becker and Co., 33 Hatton Wall, London, E.C.).

It is a perfectly colourless liquid, practically unalterable by light (I have exposed some to sunlight for a whole summer without more than a trace of yellow colour appearing). It has a characteristic but not disagreeable smell like that of ordinary mustard oil; when warmed, however, rather pungent vapours are given off. Its boiling point is very high ($222^\circ C.$), and it is not readily inflammable,—in fact, a lighted match may be thrown into it without setting it on fire.

I have determined carefully the indices of refraction for the principal Fraunhofer lines. For sodium light, $\mu_D = 1.654$ at $10^\circ C.$; and its dispersive power is rather higher than that of carbon disulphide, viz. $(\mu_{\gamma} - \mu_{\alpha}) = 0.060$. These high refractive and dispersive powers are attributed by Dr. Gladstone† to the presence of the phenyl radicle and the sulphur atom in it, both of which have a very high specific refractive energy.

It is evident from what has been said that phenyl-thiocarbimide possesses all the good qualities of α -monobromonaphthalene and of carbon disulphide, without the yellow colour and doubtful permanency of the first, and the dangerous inflammability and volatility of the second. I have used it in a prism belonging to my spectrometer for many years, and found it very satisfactory in every way, giving excellent definition (especially in the more refrangible part of the spectrum), and being much less liable to disturbance by internal convection currents than carbon disulphide. I have also made a polarising prism on Jamin's principle,—a thin plate of Iceland spar placed obliquely in a cell filled with phenyl-thiocarbimide,—and found it to answer well; though of course a solid prism is preferable, as long as pieces of Iceland spar of sufficient size can be obtained.

Phenyl-thiocarbimide readily dissolves meta-cinnamene, forming, when equal weights of the substances are taken, a viscous mass like Canada balsam, having an index of refraction about the mean of the two constituents ($\mu_D = 1.63$ at $15^\circ C.$). This does not harden so readily as balsam, but in all other respects it seems excellently fitted for use in mounting microscopic objects.

* 'Proceedings of the Royal Society,' ix. p. 256.

† 'Journal of the Chemical Society,' xlv. p. 241.

I have tried the solubility of phosphorus in phenyl-thiocarbimide, but I find it to be very slight, except while the solvent is hot; on cooling, the greater part of the phosphorus is precipitated again.

6. *Piperine* (formula of molecule, $C_{17}H_{19}NO_3$). This, like quinine, is a substance so strongly imbued with what perhaps I may call the "original sin" of crystallisability, that until lately I never thought it worth examination.

It is, as its name implies, the alkaloid existing in ordinary pepper, from which it may be extracted by alcohol. It occurs in commerce as yellowish-white monoclinic prisms, isomorphous with those of quinidine, but containing no water of crystallisation. When heated, the crystals begin to melt at $135^{\circ}C$., forming a yellowish slightly viscous liquid, which solidifies into a light yellow tough transparent resinous mass, soft enough to be easily indented with the finger-nail, and rather "tacky." This resin-form of piperine when heated to $100^{\circ}C$. is converted (like quinidine, but not quite so readily) into a white mass of crystals, which on further heating melt at $135^{\circ}C$., passing into the resinous condition. If the temperature is raised still further, at about 200° the substance begins to decompose, and the liquid becomes dark yellow or brown, owing to separation of carbon.

Resinous piperine has, unlike quinidine, very strong cohesive properties, and does not give the slightest trouble by cracking under mechanical stress or thermal changes, even when in thick pieces. I find its refractivity to be remarkably high, its index of refraction for yellow sodium light being 1.681 at 18° ; but its dispersive power is more remarkable still, the coefficient of dispersion being no less than $(\mu_{n_{\gamma}} - \mu_{n_a}) = 0.141$. I have not yet determined the indices for a sufficient number of wave-lengths to enable me to state exactly where the greatest extension of the spectrum takes place, but it is certainly in the part including the shorter waves, corresponding to green and blue (as in the case of carbon disulphide).

It will be seen from the above-mentioned properties that piperine would serve admirably for a cement and mounting material, if it were not for its suspicion of crystallisability and its abnormal dispersion. Both of these defects seem likely to be lessened by admixture with other more orderly materials, and the most promising which I have tried at present is Canada balsam. A mixture of four parts (by weight) of piperine with one part of balsam has a refractive index for yellow sodium light of 1.657 at 16° , and a coefficient of dispersion of 0.130 . The tendency to pass into the crystalline condition when heated to 100° seems greatly lessened, though not removed altogether.

One other point I would notice with regard to piperine (and quinine also) for the purpose of eliciting the experience of others. I am inclined to think that the tendency towards crystallisation becomes greater when the resin-form has been once or twice re-melted. It is well known that some kinds of glass, especially the German "soft

soda-glass," behave in a similar way, becoming semi-opaque or "devitrified" when heated to the softening point and retained long in that condition, owing to the formation of crystalline silicates in the colloidal mass.

7. *Methylene di-iodide* (formula of molecule, CH_2I_2), discovered as long ago as 1858 by Butlerow.*

This is in several respects a very remarkable substance, and I am surprised that, while it has been known and used for many years by mineralogists on account of its high density,† it does not appear to have attracted the notice of microscopists.

It is, when pure, a pale yellow liquid with a slight sweetish smell, boiling at 181°C ., freezing at 5°C ., and hardly at all inflammable, at any rate at ordinary temperatures. Its density is no less than $3\cdot34$ times that of water, so that nearly all kinds of glass, as well as most minerals (even fluor spar and hornblende) float in it.

Its refractive and dispersive powers have been accurately determined by Dr. J. H. Gladstone,‡ who finds its index of refraction for yellow sodium light to be $1\cdot756$ at $10\cdot5^\circ\text{C}$. My own examination of a different sample gives $1\cdot743$ at 15°C .,—a very close agreement when the correction for decrease of refractivity with temperature is made. This, it will be observed, is exceptionally high, in fact the highest of any single organic substance I have met with, and induces me to recommend methylene di-iodide (which is easily procured commercially) as a temporary mounting medium. I regret that I must say "temporary" only; for like many other iodides it has a slight tendency to decompose, especially when exposed to light, with liberation of iodine, which colours the liquid red, and would act upon and damage some delicate tissues and crystals. I find that after one hour's exposure to direct sunlight the liquid becomes perceptibly darker, and four hours' exposure turn it a light orange about the tint of "golden sherry." Another day's exposure to ordinary daylight only deepens the colour slightly, and after a week's exposure the liquid is still only light red, a tint hardly perceptible in thin films. In the dark it may be kept for years without alteration, and the free iodine may at any time be readily removed by shaking up the liquid with dilute solution of potassium hydrate ("caustic potash"), allowing it to stand, decanting off the potash, and removing the last traces of moisture by leaving a lump of calcium chloride in the liquid for a short time. Most of the colour may be removed more simply, but more slowly, by placing a strip of zinc in the liquid for a day or two.

One drawback to the use of methylene di-iodide is that it freezes, as already mentioned, at a point a little above the freezing point of water. This, however, can be prevented by adding to it about one-

* Comptes Rendus, xvi. p. 595.

† 'Neues Jahrbuch für Mineralogie,' 1886, ii. p. 72; 1888, i. p. 213; 1889, ii. p. 185.

‡ 'Journal of the Chemical Society,' lix. p. 293.

third its volume of phenyl-thiocarbimide. The refractivity is, of course, slightly lowered thereby, but the mixture remains liquid at a temperature at least as low as -12° C.

The coefficient of dispersion of methylene di-iodide is ($\mu_{\text{H}\gamma} - \mu_{\text{H}\alpha} =$) 0.062 , nearly the same as that of phenyl-thiocarbimide, and decidedly higher than that of carbon disulphide.

8. *Solution of sulphur in methylene di-iodide.*—When heated, methylene di-iodide dissolves a considerable quantity of sulphur, but much of this crystallises out on cooling. Sufficient, however, remains in solution at ordinary temperatures to raise the index of refraction of the liquid to 1.778 (at 16° C.) for yellow sodium light.

9. *Solution of phosphorus in methylene di-iodide.*—This solution seems worthy of special attention as a substitute for the solution in carbon disulphide sometimes employed. I find that methylene di-iodide dissolves phosphorus very freely, in fact it will dissolve its own weight of the element without reaching the point of saturation. The refractivity of the light yellow solution thus obtained is, as might be predicted, very high indeed. I find the index of refraction for yellow sodium light to be 1.95^* at 18° C., and the coefficient of dispersion is ($\mu_{\text{H}\gamma} - \mu_{\text{H}\alpha} =$) 0.092 .

The solution is far safer and pleasanter to deal with than phosphorus itself or its solution in carbon disulphide. I have poured some on filter paper and left it freely exposed for hours and even days, without its catching fire. I have left some similarly exposed in a watch-glass for a week without inflammation taking place. The scarcely inflammable solvent seems to form a kind of varnish over the phosphorus which protects the latter from rapid oxidation. Still the precaution of having a basin of water and a wet cloth at hand should not on any account be neglected in dealing with the solution.

Light acts strongly and inevitably on this medium, as on phosphorus itself and other preparations containing it, causing the conversion of the phosphorus into the allotropic form known as "red phosphorus," which is insoluble and nearly opaque. Hence such substances can only be considered available for temporary purposes, where their very high refractivity enables critical points of structure to be made out with greater distinctness. In the dark they keep fairly well, but a slight red deposit is liable to form.

I have now brought before the Society the principal substances which I have examined at present. None of them, it will seen, come up to a high standard of excellence as mounting and cementing media; but I still hope that I or others may discover something

* I do not give the third decimal place owing to a remarkable and not easily explicable difficulty which occurs in getting a sharp image of the spectrometer slit through the solution. The same difficulty was noticed by Dr. Gladstone and Mr. Dale in examining the refractivity of solutions of phosphorus in carbon disulphide. ('Philosophical Magazine,' [4] xviii. p. 30.)

better. The most hopeful direction in which to look is towards compounds containing either or both of the radicles naphthyl and phenyl, in which, as Dr. Gladstone's researches have shown, the carbon-atoms are so situated in the molecule as to cause exceptionally high refractivity in the resulting compound.

TABLE OF OPTICAL CONSTANTS OF SOME HIGHLY REFRACTIVE ORGANIC SUBSTANCES.

Name of Substance.	* μ_{H_α}	μ_D	μ_{H_β}	μ_{H_γ}	Temp. Cent.	Coefficient of Dispersion ($\mu_{H_\gamma} - \mu_{H_\alpha}$).
Meta-cinnamene (or Metastyrol)	1.592	1.597	1.612	1.624	15	0.032
Quinidine	1.596	1.602	1.621	1.639	15	0.043
Phenyl thiocarbimide	1.646	1.654	1.681	1.706	10	0.060
α -Monobromonaphthalene† ..	1.649	1.658	1.682	1.704	20	0.051
Naphthyl-phenyl-ketone	1.659	1.669	1.697	†	15	..
Piperine	1.665	1.681	1.734	1.806	18	0.141
Methylene di-iodide	1.732	1.743	1.767	1.794	15	0.062
Solution of sulphur in methy- lene di-iodide	..	1.778	..	..	16	..
Solution of phosphorus in me- thylene di-iodide (equal weights of each)	1.929	1.944	1.984	2.021	18	0.092

* The observations of the hydrogen lines were made with an "end-on" vacuum tube, a form which was first proposed by Prof. Piazza Smyth, and which gives a remarkably brilliant hydrogen light.

† B. Walter, Ann. Phys. und Chem. [N.F.], 1891, p. 511.

‡ It was found impossible to observe H_γ , owing to the strong absorptive power of the substance for the more refrangible part of the spectrum.