

alter on cooling ; after standing 24 hours the upper layer of acid for a depth of about one centimetre from the surface had become colourless ; but at the end of five months the acid in the lower part of the tube was still pink, the upper half having become colourless, and a small quantity of a black powder having settled at the bottom.

Only a very small quantity of iodine can be held in solution by the hydrogen sulphate when cold, as any excess separates out in minute crystals.

It does not appear probable that the difference in the colour of the solutions which iodine forms with liquids of these two classes depends on any chemical fact, as both classes contain substances of very dissimilar chemical composition. I have not, however, as yet been able to ascertain any common property possessed by all the liquids of either class, beyond (as, indeed, is obvious) that all those in which iodine forms violet solutions are volatile liquids of high specific gravity.

It has been shown by various observers (H. Morton, Pogg. Ann. vol. clv. p. 573 ; Hagenbach, Pogg. Ann. vol. cxlvi. p. 533 ; Kraus, 'Chlorophyllfarbstoffe,' p. 53) that the position of the absorption-bands of substances in solution vary to a certain extent with the liquid in which they are dissolved ; but this would appear to depend on some other cause ; for, in addition to the displacement being small, it differs in amount with different liquids ; whilst in the case of iodine, as far as I have been able to observe, the position of the absorption is the same for all the liquids belonging to one of the two classes. The action on light of iodine dissolved in alcohol greatly resembles the effect it produces when in the solid state ; whilst the absorption of its solution in carbon bisulphide, and in other liquids of that class, bears, as has been pointed out to me by Professor Stokes, the same relation to the absorption-spectrum of the vapour as the spectrum of the solution of a coloured gas (nitrogen peroxide for example) does to that of the gas.

II. "On the Polarization of Light by Crystals of Iodine." By Sir JOHN CONROY, Bart., M.A. Communicated by A. G. VERNON HARCOURT, Lee's Reader in Chemistry in the University of Oxford. . Received April 12, 1876.

On examining by means of a Nicol prism the light reflected from the surface of a layer of iodine, obtained by heating a fragment of that substance and then squeezing it between two plates of glass, as described in the preceding paper, I found that the film did not appear of uniform brightness, and that when the Nicol was rotated the relative brilliancy of different parts of the film changed—a portion that had appeared dark when the principal section of the Nicol was vertical, became bright when it was horizontal, and *vice versa* ; and, also, if instead of altering the

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position of the Nicol, the film of iodine was rotated horizontally, the Nicol remaining at rest, the same changes in brilliancy occurred.

Removing the upper glass made no difference, except that the surface of the film of iodine tarnished rapidly, and then the amount of light reflected by it became considerably less.

The light incident upon the surface of the iodine was either ordinary diffused daylight or the light of a paraffine-lamp; and in neither case did it show more than the merest trace of polarization, and generally not even that, when examined by means of a double-image prism and a plate of selenite.

It therefore appears that the light reflected from the surface of a layer of iodine is polarized, and that the position of the plane of polarization is not, of necessity, either parallel or perpendicular to the plane of incidence, but bears a definite relation to some direction within the crystals composing the film.

I also found that when these films were sufficiently thin to be transparent the light they transmitted was polarized, and that the plane of polarization of the transmitted light was perpendicular to the plane of the light which was polarized by reflection from the same portion of the film.

After making these observations I ascertained that W. Haidinger had announced, upwards of twenty years ago (Pogg. Ann. clxxi. p. 321, 1847), that the surface-colours which certain substances show by reflected light, in the case of some of the platino-cyanides, namely, those of potassium, barium, and magnesium, consist partially of light polarized in a plane which bears a definite relation to the axis of the crystal; and in a subsequent paper (Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, viii. p. 97, 1852) he states that certain other substances have the same property. He mentions iodine in this latter paper as showing these "surface-colours," but does not appear to have noticed that the plane of polarization of the light reflected from its surface bore any relation to some fixed direction within the substance.

I arranged a form of polariscope by means of which these observations could be repeated with a greater degree of accuracy. The instrument used consisted of a divided brass circle fixed vertically to a firm support; a Nicol furnished with a graduated circle was carried by an arm moving round the centre of the circle, and the slip of glass with the layer of iodine rested horizontally on a stage at the top of a tube, the height of which could be adjusted so that the surface of the iodine was level with the centre of the graduated brass circle. Both the stage and the tube revolved horizontally, and could be rotated independently of each other; and the latter had an index moving over a divided circle attached to it, and a diaphragm with an opening about 6 mm. wide fixed in it. By altering the position of the arm moving over the vertical circle the light reflected from the surface of the iodine at different angles could be ex-

aminated; and by reflecting light along the axis of the tube, by a mirror placed below it, and clamping the arm in such a position that the axis of the tube and Nicol were in the same straight line, the polarization of the light transmitted by the iodine could also be observed. A second or polarizing Nicol was so arranged that it could either be brought below the tube or placed between the surface of the iodine and the source of light, so that the behaviour of the film, when the incident light was polarized, could be studied.

On repeating the before-mentioned observations with reflected light I found that occasionally portions of the film of iodine appeared quite black in certain positions of the film and Nicol, and that these same portions, when examined by transmitted light, did not merely alter in colour as the film or Nicol was rotated, as the remainder did, but in certain positions transmitted no light at all—or, in other words, that they behaved in a similar manner to what a plate of tourmaline would have done; and when seen by ordinary light and the naked eye, although they appeared to be of the same thickness as the remainder of the film, by which they were wholly or partially surrounded, they were of a much paler colour; usually, moreover, they reflected rather less light than the rest.

The change in the appearance of these portions of the film when seen through a Nicol was very striking in the case of some of the larger ones, as in certain positions they appeared perfectly transparent and of a pale yellow colour, and objects situated behind them could be clearly seen; but on turning either the film or the Nicol they became perfectly opaque, and resembled highly polished metallic surfaces.

On examining one of these films of iodine with a microscope with a $\frac{2}{3}$ object-glass I found that those portions of the film which polarized light most strongly differed considerably in appearance from the remainder, and that they appeared to consist of long crystals about $\cdot 003$ inch wide adhering together side by side, whilst the rest of the film seemed to consist of thin plates of iodine overlaying one another, these, also, being long in proportion to their width.

A Nicol prism was placed over the eyepiece, and I then found that when the principal section of the Nicol was perpendicular to the long axes of the crystals, the maximum amount of light was transmitted, and when the principal section was parallel with the long axes of the crystals, they either appeared perfectly opaque or transmitted the minimum amount of light, according as the crystals in the field of view belonged to one or other class.

Other specimens of iodine showed this crystalline arrangement with different degrees of distinctness; but in all, or nearly all, some trace of it could be seen. In some cases, however, the minimum amount of light was transmitted when the principal section of the Nicol was not parallel with what appeared at first sight to be the long axes of the crystals; but

a more careful examination usually showed some traces of crystalline structure in a direction parallel with the principal section of the Nicol.

I shall refer to these two forms of iodine as iodine α and iodine β , calling those portions of the film α which are of a darker colour and polarize the light imperfectly, and the light-coloured strongly polarizing parts β .

From the appearance of the film, when seen under the microscope, it appears probable that this difference depends merely on the arrangement of the crystals, and that when they are regularly disposed in a single layer the film is one of those which I have called iodine β ; whilst iodine α consists of several layers of thin crystals lying in various directions, or it may be due to different faces of the crystals of iodine being in contact with the glass, and to the light passing through the crystals in a different direction.

The difference between the action of the crystalline film on the transmitted light is one of degree only; for I obtained two specimens of iodine β in which the film was of unequal thickness; and in this case, when the principal section of the Nicol was parallel with the long axes of these crystals, the thick portion of them appeared opaque, but a considerable amount of light was transmitted by the thinner portions of the very same crystals. Moreover several specimens of iodine β which appeared perfectly opaque in certain positions of the Nicol when seen by ordinary daylight, were of a deep red colour when examined by direct sunlight; and I have recently succeeded in preparing several films of iodine β so thin that they were only opaque when seen through a Nicol, whose principal section was parallel with the length of the crystals, with very weak light; by ordinary daylight they appeared of a deep red colour under these circumstances.

Iodine α .—Films of iodine α between two slips of glass were laid on the stage of the polariscope, and the light they transmitted examined with the analyzing Nicol; on turning either the stage or the Nicol, the colours of the film varied, according to their thickness and the relative positions of the film of iodine and the Nicol, from a kind of brownish yellow to a deep red, the colours being similar to those of solutions of iodine in alcohol of various strengths.

When the incident light was polarized, and the film of iodine placed so as to transmit the minimum amount of light, or at right angles to this position, the field was dark when the Nicols were crossed and light when they were parallel. When, however, the film of iodine was in an intermediate position, the field was no longer dark in any position of the analyzer, the colour and intensity of the light varying slightly as it was turned.

Iodine β .—A film of iodine β of a yellowish brown colour was examined by transmitted light; the field appeared perfectly dark in two positions of the film and Nicol. With polarized light, when the film was

placed at right angles to the position in which it transmitted no light, the field was dark when the Nicols were crossed and light when they were parallel. When, however, the iodine film was placed in an intermediate position, the field was no longer dark when the Nicols were crossed, though it was so in two positions of the analyzer 180° apart.

In order to simplify the description of the experiments, I shall speak of the direction in the film which, when placed parallel with the principal section of the Nicol, caused the field to appear dark, or in the case of iodine α to be least bright, as the axis of the crystal.

Very thin films of iodine β , as I have mentioned before, are not opaque when the principal section of the Nicol is parallel with the length of the crystals, and, when examined with the polariscope, appear of a deep red colour, when, under similar circumstances, a thicker film would transmit no light at all.

Hence it would appear that iodine belongs to the class of double refracting substances in which the coefficient of absorption differs according to the direction in which the light passes through the crystal, and, further, that the ray whose plane of polarization is perpendicular to the axis of the crystal is most energetically absorbed.

This is the case with both forms of the crystalline layer of iodine; but the two rays are much more unequally absorbed by iodine β than by iodine α —so much so that whilst the latter only appears absolutely opaque when the principal section of the Nicol and the axis of the crystal are parallel, when the film is so thick that but little light can pass through under any circumstances, the former absorb the one ray so energetically that a layer which appears light yellow when the Nicol is in one position is absolutely opaque when it is turned through an angle of 90° .

When a thin film of iodine β is seen through a Nicol whose principal section is so placed that the minimum amount of light is transmitted, the light usually appears of the same colour and brightness as that which has passed through the adjacent portions of the film consisting of iodine α ; and it is impossible to see where one form of the film ends and the other begins. From this it would appear as if both forms of the crystalline layer absorbed light polarized in a plane perpendicular to the axis of the crystals with equal intensity, but that they differ greatly in their absorptive powers for light polarized in a plane at right angles to this.

I have shown, in the preceding paper, that solutions of iodine in alcohol, when seen by transmitted light, vary in colour, from a pale yellow to a deep red, according to the strength of the solution and the thickness of the layer through which the light has to pass. In a similar manner, in proportion as the thickness of the films of iodine increases, the light becomes more and more red; and four films of iodine β , which when seen separately were of a pale yellow, appeared of a deep red when super-

imposed, and so placed with respect to each other that they transmitted the maximum amount of light.

The light of a paraffine-lamp reflected from the surface of a film, consisting partly of iodine α and partly of iodine β between two slips of glass, was examined by means of the Nicol, the angle of incidence being about 60° .

When the principal section of the Nicol was in the plane of incidence, and when consequently but little of the light reflected from the surface of the glass was transmitted, portions of the film of iodine appeared of different degrees of brightness; and on rotating either the Nicol or the stand, the relative brilliancy of different portions of the film changed, those portions which consisted of iodine β appearing perfectly black in certain relative positions of the film and Nicol, whilst the remainder of the film merely became more or less bright.

The film of iodine was then placed so that the portion consisting of iodine β appeared perfectly black when the principal section of the Nicol was in the plane of incidence. On rotating the stand, light reflected from the surface of the iodine was transmitted by the Nicol, and increased in quantity till the stand had been turned through 90° , when the surface of the iodine had a brilliant metallic lustre. On continuing the rotation, the surface gradually lost its brilliancy, and when the stage had been turned through 180° appeared perfectly black again.

On rotating the Nicol the same changes took place; but the light reflected from the surface of the glass marked the effect to a considerable extent when the principal section of the Nicol was no longer in the plane of incidence.

The light incident upon the surface of the glass showed no signs of polarization when examined by a double-image prism and plate of selenite, and only the faintest trace of it after passing through, at an angle of about 60° , a slip of glass similar to those used for covering the layers of iodine; consequently the polarization of the light must be due to the film of iodine.

From this it appears that the light reflected from the surface of a film of iodine β is polarized; and by examining the light transmitted by the same portion of the film, it was ascertained that the plane of polarization of the reflected light is perpendicular to that of the ray which is most freely transmitted, and consequently that the reflected light is polarized in a plane at right angles to the axis of the crystals.

When the incident light was polarized, it was found that it was reflected from the surface of the iodine when the plane of polarization of the light was perpendicular to the axis of the crystals, and extinguished when parallel.

As has been stated before, when a film of iodine α is seen through a Nicol, it does not appear black in any position; but the brilliancy of the surface alters as the Nicol or iodine is rotated.

Experiments similar to those just described show that when a ray of plane polarized light is incident upon such a surface of iodine, it is never completely extinguished, as is the case with iodine β ; but the intensity of the reflected light depends on the relative position of the plane of polarization and the axis of the crystals, being least when they are parallel.

When the slips of glass between which the iodine has been melted are carefully separated, the film usually remains attached to one of them in a sufficiently perfect condition to be examined. At first it is extremely brilliant, and shows exactly the same appearances as have already been described as occurring with film of iodine under glass. The surface, however, not only tarnishes rapidly, but even at a low temperature (10°) the film quickly evaporates; and consequently the uncovered films are somewhat difficult to examine.

They, however, permit some additional facts to be observed, which either are seen with difficulty or not seen at all when the iodine is covered with a plate of glass: and chief amongst these is the "surface-colour" which iodine shows when light is incident upon it at a high angle.

When a film of either iodine α or β is placed on the stage of the polariscope with its axis parallel with the plane of incidence and the principal section of the Nicol in the same plane, the surface of the iodine appears bright and metallic when light is incident on it at an angle of about 60° . As the angle of incidence increases, the colour of the reflected light changes; at about 70° the surface appears blue, and is still bright, but has lost its metallic appearance to a considerable extent, and at about 72° the colour is most intense; but as, in addition to the difficulties which are inseparable from determinations of this kind, the instrument which I have used for these experiments does not allow of any very accurate measurements being made with it, the value of these angles can only be regarded as approximate.

On rotating the stand the amount of reflected light diminishes rapidly, and the iodine appears dark or nearly so when the axes of the crystals are perpendicular to the plane of incidence.

On rotating the Nicol, the axes of the crystals of iodine remaining parallel with the plane of incidence, the surface of the iodine becomes bright and metallic, the maximum amount of light being transmitted when the principal section of the Nicol is perpendicular to the plane of incidence.

When the incident light is polarized in the plane of incidence the surface of the iodine appears brilliant and metallic in all positions, and when seen through the analyzer the amount of light reflected by the film alters as the former is rotated, but there is no trace of colour.

When, however, the light is polarized perpendicularly to the plane of incidence the reflection from the surface of the iodine is a coloured one

when the axes of the crystals are parallel with the plane of incidence ; consequently the appearance of the film is exactly the same when unpolarized light falls on its surface and it is seen through a Nicol whose principal section is vertical, and when the incident light is polarized perpendicularly to the plane of incidence and it is seen directly.

These experiments show that when light falls upon the surface of a film of iodine at an angle of about 72° a portion of the light is polarized by reflection in the plane of incidence, and this independently of the position of the crystals composing the film, and that another portion of the light, which is coloured by reflection, and to which the surface-colour is due, is polarized in a plane whose direction depends on that of the crystals composing the film, and, further, that this light is polarized perpendicularly to the axis of the crystals.

The surface-colour can only be seen when the angle of incidence which the light makes with the surface of the iodine is a large one ; and the reason that in the case of iodine covered with glass it is not visible, apparently is, that with a large angle of incidence nearly the whole of the light is reflected from the surface of the glass. I succeeded in seeing the blue colour in the case of a fragment of iodine which had been melted between a slip of glass and one of the sides of a small crown-glass prism of an equilateral section, and also when such a prism was placed on the surface of one of the glass slips covering the iodine, a drop of carbon tetrachloride (the index of refraction of this liquid being nearly the same as that of the glass) being placed between the slip and the prism, as under these circumstances light can reach the surface of the iodine at a greater angle than is possible when it is covered by a flat piece of glass ; but in neither case was the surface-colour so well seen as when the iodine was uncovered.

Haidinger has remarked (*Sitzungsberichte der kaiserlichen Akademie der Wissenschaften*, Band viii. p. 97) that the surface-colours are complementary to the colour of the light transmitted by the same substance ; and this also appears to be the case with iodine, as in the solid and liquid condition, and also when dissolved in certain liquids, it absorbs most readily the blue rays ; but at the same time, as Professor Stokes has pointed out, the surface-colour and the colour of the transmitted light can only be said to be complementary within very narrow limits, as the colour of the transmitted light varies with the thickness of the layer of substance through which it passes.

Films of iodine α and β , when the light was incident on their surface at a considerable angle, were found to polarize the light elliptically in certain positions of the film, as was shown by the black cross being distorted when a plate of Iceland spar, cut perpendicularly to the axis of the crystal, and a plano-convex lens of about 40 mm. focal length were placed between the surface of the iodine and the analyzing Nicol. The amount of distortion, which was never very considerable, increased

with the angle of incidence, and appeared to attain its maximum when the angle was about 72° .

When a film of either iodine α or β is placed on the stage with its axis perpendicular to the plane of incidence, and the principal section of the analyzer parallel with the latter plane, the black cross is perfect; but on turning the film till its axis is parallel with the plane of incidence, the cross becomes slightly distorted, and the centre appears bluish. When the light falling on the surface of the film is polarized in a plane forming an angle of 45° with the plane of incidence, the principal section of the analyzing Nicol still remaining in that plane, the black cross is perfect as long as the axis of the iodine is perpendicular to the plane of incidence, and distorted when it is parallel.

Iodine β only shows the black cross very faintly with unpolarized light when its axis is perpendicular to the plane of incidence.

The distortion when the incident light is polarized is far greater than that produced by the reflection of a ray of light, polarized at an angle of 45 degrees with the plane of incidence, from the surface of a piece of glass, and quite comparable in amount with the effect produced when the light falls on a metallic surface.

I selected from a large quantity of freshly sublimed iodine a few pieces bearing a more regular crystalline form than the rest, and amongst these there were two nearly triangular plates, about 10 mm. long and 8 mm. broad.

One of these was arranged on the stage of the polariscope, and the light reflected from the surface observed in the way that has already been described in the case of the films of iodine.

The light was most completely polarized when the angle of incidence was about 72° ; when the length of the crystal was perpendicular to the principal section of the analyzer it appeared darkest, and when parallel with it lightest.

The surface-colour and the distortion of the black cross were as clearly seen as with the film of iodine.

After several unsuccessful attempts I succeeded in preparing some well-defined crystals of iodine by carefully heating on a sand bath a small quantity of that substance in a wide-mouthed stoppered bottle, when some perfect rhomboidal plates of iodine about 1 mm. long were deposited on the cool part of the bottle. When these were examined with the polariscope, the principal section of the Nicol being in the plane of incidence, they appeared brightest when their long axis was parallel with, and darkest when it was perpendicular to, the plane of incidence.

Hence it appears that when the long axes of these crystals are parallel with or perpendicular to the plane of incidence, part of the light reflected from their surface is polarized in the plane of incidence, and part in a plane at right angles to their long axes, and consequently that the long

axes of these rhomboidal plates correspond with that direction within the film of iodine which has been spoken of as the axis of the crystal: and as iodine belongs to the trimetric system, this may be considered the principal axis, as being the one in the direction of which the crystals are prismatically developed to the greatest extent; and it also appears that when a ray of light passes normally through such a crystal it is divided into two rays polarized respectively parallel with and perpendicular to the same axis; and the one whose flame of polarization is parallel with the principal axis suffers the least absorption.

III. "*Picrorocellin*." By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES EDWARD GROVES. Received April 27, 1876.

Through the kindness of Mr. C. Lavers Smith, the eminent orchil manufacturer of Spitalfields, we were furnished with a quantity of a lichen which he had observed to have a very bitter taste, and which came into the market through a Portuguese house. It is believed to have been brought from the West Coast of Africa; but our endeavours to ascertain the exact locality have hitherto been unsuccessful. From the appearance of the lichen it seems to grow on limestone rocks; and Mr. W. Carruthers, of the British Museum, and the Rev. J. Y. Crombie, to whom we submitted it, pronounced it to be a variety of *Rocella fuciformis*, the ordinary *Rocella* usually growing on trees. This lichen is remarkable for its intensely bitter taste; and the preliminary experiments showed that this is due to the presence of a crystalline compound which is but slightly soluble in water.

Picrorocellin.

The lichen was accordingly first treated with water and hydrate of lime, in the usual manner, to extract the erythrin which it contains in common with other varieties of *Rocella*, and the residue, after being dried at the ordinary temperature, was extracted by boiling spirit. The alcoholic solution, which contained the bitter substance together with chlorophyl and various fatty and resinous impurities, was concentrated by distillation until almost the whole of the alcohol was removed. When cold, the dark-coloured pasty mass was pressed in a cloth, boiled up with a small quantity of strong spirit, and allowed to cool, pressed, and again treated in the same manner. By this means much of the chlorophyl and almost the whole of the oily matters were dissolved out, leaving a dark green-coloured crystalline product. In order to remove the last traces of chlorophyl from this, it was boiled up twice or thrice with benzine, in which the crystals are only slightly soluble.

The spent "weed" from this variety of lichen which has been exhausted with ammonia in the ordinary process of the orchil manufacture also yields the same crystalline substance, but it is much more difficult to purify