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The existence of reversible photosensitivity in some artificial materials containing rutile.

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Introduction.

IN 1934 a contribution from America (Parmelee and Badger, p. 2) reported that a certain glaze, containing rutile, showed rapid reversible darkening in daylight. It was stated that C. H. Zwermann, Jr., ascribed this photosensitivity to titanium. In the present author's experience the phenomenon is often exhibited, in varying degrees, by commercial glazes based on rutile or on the purified titanium dioxide available in industry, as well as by glazes made up in the laboratory from chemical titanium dioxide of high purity. Lee, also in America, observed reversible darkening in sunlight in commercial titanium dioxide itself, and the existence of this effect was confirmed by Williamson (1937) for some brands of commercial titanium dioxide available in Britain. These brands were affected by daylight which had passed through glass, and some tentative suggestions were made regarding the mechanism of the reversible darkening. Later it was demonstrated (Williamson, 1939) that reversible darkening in daylight could be produced in a sample of titanium dioxide of considerable purity, which was itself not discoloured by light, by contamination with iron according to a special method. This sample of titanium dioxide had the following spectrographic analysis (prepared by Messrs. Adam Hilger, Ltd.): Ca, trace; Fe, very slight trace; Na, very slight trace, practically nil; P, trace; Pb, minute trace, practically nil; Sb, slight trace; Si, heavy trace; Sn, minute trace.

Elements sought with negative result: Ag, Al, As, B, Ba (probably; lines masked), Be, Bi, Cd, Co, Cr, Cu, K, Li, Mg, Mn, Mo, Ni, Sr, Th, Tl, V, W, Zn, Zr. The same sample has been used throughout the present work. It is also to be understood that any darkening of titanium compounds which may be mentioned occurs in daylight, not direct sunlight, which has passed through glass, and that, unless otherwise stated, the titanium compounds have been confined in such a way that they exhibited the same portions of particle surfaces to the light during the period of illumination (cf. Williamson, 1937).

Three types of photosensitive titanium preparations are subsequently described. They are termed, for convenience, A, B, and C, and consist partly or wholly of rutile. No attempt has been made to obtain a quantitative idea of the photosensitivity, and all three preparations are too fine-grained to show this effect on other than bulk samples.

Type A.

Preparations of Type A were made according to the method already outlined (Williamson, 1939). Titanium dioxide was mixed with an aqueous solution of an appropriate salt of analytical reagent quality, evaporated to dryness, ground, and calcined in a metallic resistance furnace which attained a temperature of 1000° C. at the end of a three hours' cycle. The resulting product was ground, if required, before study, but usually only a feeble suggestion of sintering was to be found.

The most strikingly photosensitive preparations obtained were those of Type A, containing a calculated ratio of 0.2 Fe₂O₃ to 100 TiO₂ in parts by weight, in which the iron had been introduced as ferrous sulphate or ferric ammonium sulphate. These preparations, after storage for some hours in the dark, showed, when, in the form of a heap of powder they were suddenly exposed to the light, a darkening which was so rapid that the eye could easily follow it without reference to any standard for colour comparison. The preparations became obviously darker in a few seconds.

Type A preparations were made also by the use of ferric oxide itself. This was thoroughly ground with the titania and the mixture calcined as usual.

The effect of varying the Fe₂O₃/TiO₂ ratio is indicated in the following table. The iron was added as ferrous sulphate in an amount calculated to give $x\text{Fe}_2\text{O}_3/100\text{TiO}_2$ in parts by weight.

The table indicates that the photosensitivity is not apparent in preparations very low or very high in iron. This may imply a failure in

the mechanism responsible for the colour changes on exposure, but there is a strong probability that the failure is, at least in part, in the observer's eyes, which cannot detect small colour differences between very pale, or between very dark, samples.

x .	Unexposed colour.	Exposed colour.
0.05	White	White
0.10	White	Very pale brown
0.20	Nearly white	Pale brown
0.40	Paler medium brown	Darker medium brown
1.00	Strong orange-brown	Strong orange-brown
4.00	Stronger orange-brown	Stronger orange-brown

Microscopic study of the initial titanium dioxide and of the Type A preparations obtained from it revealed little of interest. The titanium dioxide grains showed no polarization colours, an effect which is probably to be connected with their minute size, but they were detected as tiny particles, which might show a feeble Brownian movement, at a magnification of 2080 diameters. Unground Type A preparations were microscopically similar, though there was a slight suggestion of sintering together of grains. Rare ferric oxide particles unconnected with titania appeared to exist. No crystalline growth on the surface of titanium dioxide particles was detected.

Fortunately, through the kindness of Mr. C. C. Paterson, the Research Laboratories of Messrs. the General Electric Co., Ltd., prepared six X-ray powder photographs of titanium-containing materials. The titanium dioxide used throughout the experimental work was revealed as anatase of an average crystal size of over 10^{-5} cm. A sample of it, calcined according to the cycle which was used in making Type A preparations, showed no new crystalline phase and, if there had been any increase in crystal size, it was not such as to be revealed by X-ray analysis. The Type A samples, however, exhibited a development of rutile. The results of the X-ray studies, which include a very approximate estimate of the amount of rutile present, are shown in the following table:

Metallic salt used.	Ratio $R_2O_3/100TiO_2$ by weight.	Amount of rutile.
1. $FeSO_4 \cdot 7H_2O$	0.2 Fe_2O_3	Not > 15-20 %
2. $FeSO_4 \cdot 7H_2O$	0.4 Fe_2O_3	30 %
3. $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	0.2 Fe_2O_3	Not > 5 %
4. $MnSO_4 \cdot 4H_2O$	0.2 Mn_2O_3	Not > 15-20 %

The equilibrium tint of the exposed sample no. 3 was paler than that of no. 1. This was perhaps to be correlated with the smaller proportion

of rutile in no. 3. The sample no. 4, containing manganese, was photosensitive also and passed, on exposure to daylight, from greyish-brown to creamy-brown. The colour change was not striking.

Samples made up from ferrous sulphate to give $0.2 \text{ Fe}_2\text{O}_3/100\text{TiO}_2$ but calcined to relatively low temperatures, e.g. from 15° to 615° C. in three hours, were nearly white, with a hint of pink when the powder was in the form of a heap. There was no photosensitivity. This may imply a lack of recrystallization. Ferrous sulphate, calcined by the side of these samples, yielded ferric oxide with traces of undecomposed iron sulphates.

When a Type A sample with $0.2 \text{ Fe}_2\text{O}_3/100\text{TiO}_2$ was held for three hours at temperatures between 1240° and 1250° C. it gave an insensitive material of orange-brown colour, somewhat sintered, with some red-brown spots (iron-oxide?). The microscope indicated recrystallization to anhedral grains, some coarse enough to show polarization colours. The appearance was similar to that of the strongly calcined titanium dioxide itself (vide infra) of which, of course, the present sample largely consisted.

The effects of certain reagents on Type A preparations.

Hot concentrated sulphuric acid effected a slow solution of Type A preparations, but the particles contained in them exhibited, before their complete disappearance, a marked fading of colour. This fading appeared both in preparations low enough in iron to be photosensitive and in those too rich in iron, i.e. too dark, for the sensitivity to be apparent. The fading is not to be attributed to reversible thermosensitivity (vide infra), as the paler colour persisted in the cold sample. It almost certainly results from the solution of an iron-rich portion of the sample and raises problems in connexion with the status of the iron concerned.

Because rutile was produced at the expense of anatase under the conditions prevailing during the calcination of the Type A preparations, it is logical to ascribe the photosensitivity to some type of rutile-iron association. Such an association may involve: (a) mechanical mixture of ferric oxide and rutile, where photosensitivity would not be expected to arise; (b) adsorption of ferric oxide on rutile surfaces; (c) the presence of iron in rutile crystals. There was some microscopic evidence that a small proportion of the iron was present as an oxide merely mechanically mixed in the preparations, but the fact that recrystallization of anatase to rutile has occurred suggests that some iron would be able to enter easily into growing rutile crystals. That photosensitivity appears on

the entry of impurities into rutile crystals will be apparent from study of subsequent portions of the paper.

There is, however, another point to be considered which concerns the rutile-anatase association. If we postulate the entry of a high proportion of the iron present into the growing rutile crystals, calculation suggests that in some cases the crystals might be so dark in colour that, in megascopic masses, we should not expect any perceptible photosensitivity. The very large specific surface, which must exist on the titania which is the basis of the Type A preparations, implies, however, that we may be concerned with a thin rutile film distributed over anatase particles. This condition would resemble the metallic oxide-kieselguhr associations investigated by Baly, Pepper, and Vernon (pp. 1169, 1172). It is possible that such a film may exhibit photosensitivity even when megascopic crystals are too dark to show it.

Type A preparations have been subjected also to attack by a stream of moist hydrogen chloride at temperatures of from 1000° to 1050° C. Prolonged treatment removed the iron and with the departure of the iron the photosensitivity disappeared and the preparation became white. Concomitantly the crystalline structure of the preparation was much modified and the sample became a mass of minute rutile prisms. If, however, the treatment was stopped before completion, photosensitive rutile crystals resulted (cf. Type C preparations).

Type B.

Type B preparations were obtained by heating titanium dioxide (anatase) in molten salt. Various methods have been employed for the synthesis of the crystalline phases of TiO_2 , or of substances thought to be them. The methods are summarized by Clarke, Doelter and collaborators, and Mellor, and some involve the use of fused salts. The use of fused sodium chloride does not, however, seem to have been recorded. The facts that sodium chloride can be obtained as an analytical reagent containing heavy metals only in traces, and that Clews and Thompson effected the conversion of quartz to tridymite in its presence (pp. 1446-1447), recommended the use of this material in the present study.

It was found that sodium chloride readily changed the titanium dioxide into new crystalline phases which included rutile. The conversion was studied in covered platinum vessels held in various temperature ranges, the lowest being about 860° C. and the highest attaining some 1190° C. The resulting titanium compounds showed, in bulk, a slow

darkening in daylight, but were too fine grained for the eye to trace this photosensitivity in individual crystals. There was some variation in the equilibrium tints of unexposed and exposed samples, but in general the change on illumination was from yellowish-white to brown of various shades. Sometimes, however, even the unexposed sample had a brownish tint and this appeared to be more common in preparations made at over 1000° C. The darkening in daylight was usually perceptible after several hours and, if the samples were exposed continuously for some days, tended to become more pronounced, as the reversal during the hours of darkness was slow.

It must be emphasized that the photosensitivity appeared in preparations to which no foreign impurity had deliberately been added. Thus, if the photosensitivity was initiated by the presence of foreign impurities, the sodium chloride or platinum were the most likely source of these. The possibility that platinum itself might promote photosensitivity was tested by making up Type A preparations in which, instead of an aqueous solution of an iron salt, platinum dissolved in aqua regia was used. Grey insensitive powders were obtained. This does not, however, prove the ineffectiveness of platinum in promoting photosensitivity, as recrystallization of the titania may be necessary and it is not known if this has occurred.

If foreign impurities function as promoters of photosensitivity, the presence of this phenomenon in Type B preparations may depend upon the vigorous recrystallization which has occurred. Impurities would easily be picked up by growing crystals and, if well distributed, they may be effective even in minute amount.

More striking photosensitivity was obtainable by the deliberate adulteration of Type B preparations with small quantities of ferric oxide. Alternatively, a sensitive Type A preparation containing iron was recrystallized instead of the usual titanium dioxide, or a certain sample of rutile was used. This rutile sample was one found to confer photosensitivity on glazes.

Sodium chloride melts were heated in electric furnaces, with metallic resistances, but for fusions to be held at low temperatures, e.g. about 860° C., the use of a gas burner was also possible. In the latter circumstance the titanium compounds were found to be very susceptible to even slightly reducing conditions which caused them to acquire a blue tint suggestive of the presence of traces of the ion Ti^{3+} . If this tint were faint the photosensitivity was not altogether obscured and the preparations darkened to a faint blue-grey on exposure. It may be recalled

that Junker (p. 101) found that carbon monoxide began to react with titanium dioxide at as low a temperature as 800° C.

The crystalline phases present in Type B preparations.

Only those preparations made from titanium dioxide and salt, without the addition of iron and other impurities, will be mentioned here. They have been examined with the polarizing microscope, while Mr. F. A. Bannister and Dr. G. F. Claringbull have kindly taken X-ray powder photographs of some of them. In general two phases can be distinguished by the microscope, though one phase may be present in too small a quantity to be apparent on the powder photograph also.

The insoluble portion of a fusion held for about eleven hours in the temperature range 890° to 910° C. showed, on a powder photograph prepared and studied by Mr. Bannister, strong anatase and weak rutile lines. With the microscope three constituents were detected (fig. 1):

(a) Unconverted grains of the original titanium dioxide which were doubtless responsible for the anatase lines. These had been out of effective contact with the molten sodium chloride and some were still small enough to show a feeble Brownian movement. They were not found in subsequent preparations where care was taken to use a large excess of sodium chloride and to see that the titanium dioxide was in effective contact with the fused salt, for example by letting it sink in small quantities through this material to the bottom of the vessel.

(b) Crystals with a refractive index well over that of methylene iodide and with strong birefringence, which formed needles or laths, striated along their length, without definite terminations. They showed straight extinction and negative elongation. Evidence is given later that these are not anatase but a sodium titanate.

(c) Lozenge-shaped tablets, striated along their length from one acute angle to the other, in which the striations were a direction of straight extinction and slow vibration. The edges of the tablets might be flattened, parallel to the striations, by the development of crystal faces, and there was sometimes a flat face bisecting the surface of the tablet from which striated planes sloped gently down on either side towards the obtuse angles of the lozenge, or towards the edges which appeared instead of these angles (fig. 1). In the absence of any phase which could be identified as rutile it was tempting to ascribe these crystals to that phase, the striations being parallel to the *c*-axis. The possibility of an association of rutile, not microscopically detectable, with the minute

anatase had also to be considered. The suggestion that the puzzling crystals were rutile was made more plausible by the existence, in some other fusions, of crystals which, by elongation in the direction of the striations and a loss of tabular habit, appeared transitional to stumpy rutile prisms.

Fortunately there was no difficulty in discriminating rutile in other preparations where it was abundant as positively elongated prisms, of varying length, often showing typical twinning, and also as numerous grains less well developed crystallographically (fig. 2). One such preparation was X-ray photographed by Dr. Claringbull and showed only the lines of rutile. Indeed, rutile may bulk so largely in some of the preparations that it is difficult to believe that it does not contribute, at least in part, to their photosensitivity. The other constituent, the compound mentioned under (b) above, varies in amount and may be very important in preparations made at high temperatures. One of these, examined by Mr. Bannister, came from a fusion held for six hours at 1145° to 1165° C., and showed lines which were not those of rutile, anatase, or brookite. A similar preparation yielded TiO_2 93.16 % and Na_2O 6.76 % on analysis. Preparations made below 1000° C. showed a greater though variable TiO_2 content. The unidentified lines in the powder photograph are thus very probably those of a sodium titanate. In the presence of titanium dioxide sodium chloride appears to suffer a preferential loss of chlorine, which is more pronounced at high temperatures, with the concomitant formation of sodium titanate. Microscopic evidence does not suggest the formation of more than one sodium titanate. The evidence of the powder photograph coupled with the low soda content of the analysed sample may imply the presence of a titanate rich in titania. Otherwise the lines of rutile might be expected on the photograph. The present sodium titanate closely resembles in habit, straight extinction, negative elongation, high refractive index and birefringence, and the fact that it is decomposed by hot concentrated sulphuric acid, the compound $\text{Na}_2\text{O} \cdot 3\text{TiO}_2$ prepared and analysed by Holmquist (pp. 211-212). The existence of this compound was confirmed by Junker. If we assume the presence of the compound in the present instance, the analysis given may be recalculated as sodium titanate 32.93 % and rutile 66.99 %. This titanate has not yet been isolated from the Type B preparations, but the possibility that it may contribute to their photosensitivity must not be forgotten. It is hoped to investigate the compound in more detail.

Type C.

These preparations provided direct evidence of the existence of photosensitivity in rutile, as only this phase has been identified in them under the microscope, where it appeared as many tiny prisms, often twinned (fig. 3). Dr. Claringbull kindly X-ray photographed one of the samples and found that the only lines given were those of rutile.

The preparations were obtained by the passage of a stream of moist hydrogen chloride for some hours over titanium dioxide held at temperatures between 1000° and 1050° C. The titanium dioxide was contained in a glazed porcelain boat, within a silica tube heated by a metallic resistance furnace. Chlorine was detected in the gases which issued from the tube, as the oxidation of hydrogen chloride, by the air also present in the apparatus, was appreciable at the temperatures involved (cf. Clews and Thompson, pp. 1443-1444). The titanium dioxide was recrystallized to rutile, which was white and showed only a suspicion of photosensitivity. Such rutile could then be contaminated by iron, when the resulting pale yellow or pale yellow-brown product was found to darken slightly after prolonged exposure to daylight. This contamination was effected in the same manner as was used for obtaining Type A preparations, i.e. the rutile was dried out with a solution of ferrous sulphate and re-heated. An alternative and better method was to mix the initial titanium dioxide with ferric oxide and pass hydrogen chloride over the heated product. The iron condensed beyond the furnace, partly as ferric chloride, but, if the reaction were stopped at the right time, the product was converted into rutile crystals containing some entrapped iron. This rutile altered slowly in daylight from dirty yellow to greyish-yellow. Photosensitive crystals which were grey with a hint of brown could also be obtained, apparently because of slight reduction. When such reduction occurred, it could be ascribed to traces of organic matter carried into the furnace from rubber tubing and corks in the apparatus for generating and washing the hydrogen chloride. The condition of these parts of the apparatus required careful attention. Titanium dioxide, with insufficient iron to colour it strongly, became a definite blue through accidental reduction. The work of Junker shows that it is to reduction, and not to thermal dissociation, that the blue colour must be related.

The production of photosensitivity in rutile crystals by permitting them to pick up impurities is reminiscent of the results of an early experiment in recrystallizing titanium dioxide in a stream of gas. Here

a graphite-titania mixture was heated in a current of moist chlorine. It yielded brown photosensitive rutile crystals mixed with ash. But, at the same time, a sample of titania without graphite was heated on the down-stream side of the reaction mixture. This became even more photosensitive than the rutile crystals just mentioned and passed from very pale brown to medium brown on exposure. It contained rutile, and some residual anatase grains, perhaps partly converted to rutile as in the Type A preparations. Presumably iron, and perhaps other impurities, carried from the graphite to the sample, initiated the photosensitive effect.



FIG. 1.

FIG. 2.

FIG. 3.

FIG. 1. Titanium dioxide recrystallized in the presence of molten salt. Many minute grains of unconverted titanium dioxide (anatase), elongated crystals of sodium titanate, and two crystals presumed to be rutile (towards top left and bottom right corners of square respectively).

FIG. 2. Titanium dioxide recrystallized in the presence of molten salt. Many elongated crystals of sodium titanate. The largest crystal in the figure, below the centre of the diagram, is also this material. Rutile forms short prisms, sometimes twinned, and anhedral grains.

FIG. 3. Titanium dioxide recrystallized, mixed with ferric oxide, in a stream of moist hydrogen chloride. Photosensitive rutile crystals, often twinned.

Reversible thermosensitivity in initial titanium dioxide (anatase) and in Type A preparations.

Lee (pp. 771-772) cites a number of compounds which exhibit reversible thermosensitivity, viz. HgI_2 , the chromates RCrO_4 where R is an alkaline earth metal, and the mineral gillespite ($\text{FeO} \cdot \text{BaO} \cdot 4\text{SiO}_2$). He points out that the mechanisms of the phenomena involved in reversible photosensitivity and in reversible thermosensitivity may well have common factors.

Reversible thermosensitivity is more familiarly shown by a number

of common metallic oxides both coloured and white, e.g. HgO , PbO , ZnO , SnO_2 , and TiO_2 . There is remarkably little information available concerning the mechanism of this physical change in oxides.

The titanium dioxide (anatase) used as the basis for the present experiments itself showed gradual and reversible colour changes on heating. The nature of these changes is indicated in the following scheme in which are listed the approximate temperatures at which particular colours prevailed:

Room-temperature	...	white.
100° C....	...	white.
250°	...	faint brown.
400°	...	faint brown with tinge of green.
450°	...	brownish-green.
600°	...	deep yellow-green with hint of brown.

As was true of the titanium dioxide used by Junker (p. 98), an irreversible darkening occurred at high temperatures. In the present instance this was connected with some type of recrystallization. After being held for three hours in the temperature range 1240° to 1250° C. the titania became slightly sintered and developed a strong greyish-yellow colour. When exposed to air, the surface of the sample had a yellower tint. The microscope indicated the presence of grains large enough to show polarization colours. The nature of the change on heating was not further investigated. The colour produced may be consequent upon alterations in grain-size, or perhaps the production of a new phase, e.g. rutile, in which foreign impurities can exert a more powerful tinctorial effect than they did in the original anatase. Strongly calcined titanium dioxide was still capable of being transformed into a photosensitive preparation of Type A.

Heating of the titanium dioxide for two hours at temperatures of 1100° to 1110° C. was sufficient for the production of a greyish powder containing small coherent masses. Individual grains in the powder were too small to show polarization colours.

There was a suspicion, which could not be confidently asserted, that strongly calcined titania developed a slight photosensitivity. If this can be confirmed, it is possible that the formation of rutile, containing impurities residual from the anatase, is involved.

Pronounced thermosensitivity was shown by the Type A preparations containing 0.2 $\text{Fe}_2\text{O}_3/100\text{TiO}_2$ and, because of the rapidity of the change on illumination, a connexion, real or apparent, with photosensitivity was easily established.

Two samples were heated in parallel, one exposed to light, and one

shielded from it. The latter could be uncovered at any instant and immediately covered again. A third exposed sample was kept at room-temperature as a check. Initially there was a strong contrast between the two samples, the exposed and the unexposed, but at 35° C. the difference was less pronounced and the heated exposed sample was paler than the sample kept at room-temperature. At 70° C. no difference could be detected between the exposed and covered heated samples. The difference reappeared on cooling.

The pale brown colour which was found in the heated sample persisted to high temperatures, but at 400° C. a strong brownish-green had become apparent.

After the exposure of samples behind red and violet filters, the sample behind the violet filter had the darker colour, i.e. the red light, like heat, effected a reversal of colour. In a qualitative though not a quantitative way this observation illustrates Lee's comment on the effect of heating solarized glasses (p. 772) ' . . . the colors excited by short wave ultra violet light were reversed by long wave radiation (heat)'.

Remarks by Smits, given in his earlier (1922) but not in his later book (1938), may be worth recalling. He states that some substances, including the so-called phototropic materials, are sensitive to foreign energy. The application of such energy, light in the present instance, leads to an end state at ordinary temperatures corresponding to a purely thermal equilibrium at another temperature (p. 178). The apparently analogous condition of the red-illuminated and heated Type A preparations may illustrate this thesis, though it is well to remember that Smits probably had in mind certain types of change in irradiated phototropic materials which may not be valid in the case of rutile.

General Discussion.

The photosensitivity of rutile resembles, sometimes strikingly, sometimes only remotely, a number of other phenomena. There is, for instance, an obvious connexion with the reversible darkening in daylight shown by some brands of commercial titanium dioxide. Such materials are likely to contain rutile (Morgan and Pratt, p. 152). The quantity of impurities in them is probably small, yet if these impurities are well distributed photosensitivity might be initiated. Recently the author has seen this sensitivity in a titanium dioxide, not of commercial, but of laboratory reagent quality, which passed on exposure to daylight from a creamy colour to pale brown. The photosensitivity of rutile has also associations with that of glazes containing titanium. It is hoped to

discuss these associations in a paper in the 'Transactions of the British Ceramic Society'. More remotely, there is a parallel in certain zircons which show rapid colour changes, slowly reversible, in sunlight (Spencer, pp. 12, 189).

Many compounds, both organic and inorganic, suffer colour changes when exposed to radiation of various kinds. The inorganic compounds include artificial substances and natural minerals. Among the latter, it is of historical interest to note, rutile was considered by Doelter (1911, p. 314) to owe its colour, probably, to radioactive materials. Some organic compounds change colour on exposure to light of certain wave-lengths, and the new colour is reversed when the compound is stored in the dark, or, better, exposed to light of certain other wave-lengths. Such compounds are said to be phototropic. Various explanations of this phototropy have been suggested. They are listed by de Gaouck and Le Fèvre (p. 1458), who have themselves elucidated the mechanism of the phototropy of certain anils. Under the heading of Phototropy the 'International critical tables' (vol. 7, p. 167) cite four inorganic compounds and one inorganic mixture, viz. CaS, SrS, Li_2NH , SnI_2 , and lithopone, so it may not be inappropriate to apply the term phototropy to the present reversible photosensitivity, especially as there is some evidence that one part of the spectrum (long waves) may reverse the colour developed by another (short waves). A striking example of phototropy in an inorganic compound was recently recorded by Hibben. Some large MgO crystals became deep purple in ultra-violet light. They decolorized spontaneously when removed from the light source, but could also be decolorized by certain antagonistic mercury lines. Heating speeded up the reversal of the purple colour (cf. Type A preparations). It was suggested that the phenomena are produced by some kind of electron migration connected with impurities in the MgO lattice.

The colour changes shown by many minerals, when exposed to heat or radiation, have been ascribed to the presence of colloidal impurities, for example by Doelter, a useful summary of whose work and opinions is given by Lee (pp. 772-773). The flocculation and deflocculation of such colloidal aggregates, which have diameters comparable to the wave-length of light, can provide a mechanism for the colour changes. For instance, Ekstein recently demonstrated the existence of colloidal particles in artificial crystals of salt, which particles diffused a colour depending on their size, by the use of the ultra-microscope and a monochromator (p. 242). Also, Friend and Allchin have lately shown the presence of gold (probably colloidal) in celestine. Red celestine contained

more gold than blue, and this more gold than the colourless mineral. Heating of the blue mineral turned it slightly pink.

Alteration in the degree of dispersion of colloidal impurities may be responsible for the photosensitivity of rutile, though some type of electron migration may be considered as an alternative. Indeed, the two conceptions are not necessarily incompatible, for, if the conditions obtaining in hydrosols are even remotely analogous to those existing where the dispersion medium is a solid, alteration in the charge of colloidal aggregates may be responsible for changes involving flocculation or deflocculation.

The development of colour in an irradiated crystal is not necessarily dependent on the presence of foreign impurities, i.e. impurities foreign in the sense that they have no part in the ideal chemical formula for the material. For instance, in alkali halides, the development of colour has been ascribed to the trapping of electrons at vacant lattice points, or to the presence of a stoichiometric excess of alkali metal. Further details may be found in an article by Mott. In the case of rutile, however, the coloration on illumination is much enhanced, and very probably initiated, by the presence of foreign impurities, including iron and manganese. Uncontaminated rutile showed only an unconfirmed suspicion of phototropy.

Of much interest in the present study are the investigations by Goodeve and co-workers of the photosensitizing activity of titanium dioxide. Goodeve (1937, p. 340) has shown that this oxide is activated by the light from a mercury arc which has been filtered through glass. Further, titanium dioxide absorbs light in the near ultra-violet which is exactly the region where it is photoactive. The titanium dioxide studied by Goodeve probably contained at least a proportion of rutile, while that used by Goodeve and Kitchener (1938 a) to effect the photosensitized bleaching of 'chlorazol sky blue FF' was almost certainly rutile. It was prepared by the hydrolysis of $TiCl_4$ which Weiser and Milligan found to yield rutile. These workers indicated, however, that titanium dioxide obtained by some processes is anatase; so it is not surprising to find that the titania used as a basis for the experiments of the present author was this phase. The possible mechanisms involved in photosensitization by solids are discussed by Goodeve and Kitchener (1938 b), and it must be borne in mind that there may be a real connexion between the photosensitizing activity of titanium dioxide and the reversible photosensitivity of rutile. In the one case energy is taken up on irradiation and made capable of effecting chemical change in

neighbouring molecular species, while in the other it is absorbed and promotes some change, which cannot be certainly specified as yet, within the crystal structure which results in an alteration in colour. It is also feasible that the part of the spectrum most effective in causing the darkening of rutile is that which promotes the photosensitizing activity of titania, viz. the near ultra-violet.

Finally, it must be stated that the possible existence of photosensitivity in anatase and brookite has not been investigated, but the occurrence of this phenomenon in rutile may be worthy of more study by research workers. Further, because of the extensive use of titanium dioxide in industry, their work might well have results extending beyond the field of pure science.

Phototropy may be found eventually in natural rutile, but most crystals are probably too dark for the effect to be detected. In the case of small detrital rutiles the author's experience suggests that photosensitivity, even if present, would not be perceived except in a concentrate containing many grains.

Summary.

Reversible darkening in daylight has been detected in three types of artificial material containing rutile:

(a) Anatase partly recrystallized by heat-treatment, under 'dry' conditions in the presence of iron or manganese, with the production of rutile. Certain iron-containing samples show a strikingly rapid darkening in daylight. This darkening is more pronounced in violet than in red light and is reversed on heating to below 100° C.

(b) Anatase completely recrystallized in the presence of molten sodium chloride. The resulting product contains rutile and a sodium titanate in varying proportions.

(c) Anatase converted into rutile by heating, in the presence of iron, in an atmosphere containing hydrogen chloride.

The photosensitivity is held to depend on the entry of impurities into the rutile crystals. Tentative explanations of it are given and the possibility of a connexion with the known photosensitizing activity of titanium dioxide is stressed.

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