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Physics. — *"A contribution to our knowledge of the solarization phenomenon and of some other properties of the latent image".* By A. P. H. TRIVELLI. (Communicated by Prof. S. HOOGEWERFF).

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I. *The image.*

In order to enquire into the density gradation a photographic plate may be exposed in two ways:

a. with constant light intensity and varying time of exposure;

b. by equal exposures, with different light intensities.

In order to eliminate the possibility of other circumstances being different, particularly those under which development is carried out, the first method has been adopted, a plate being divided into strips, and each succeeding strip receiving a longer exposure than the preceding one. This is combining several trial plates into one. In my opinion an "image" cannot be said to appear in this case, it only appears if the second method is adopted.

The results obtained by equal exposures with different light intensities I will call *copies*. A copy always shows an image, which may be positive or negative.

By a *normal* or non-polarized copy I understand copying positive-negative-positive- etc., which may be represented by

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By a *polarized* copy I understand copying positive-positive-etc. or negative-negative- etc., which may be represented by

$$\pm \rightarrow \pm$$

According to the investigations of WARNERKE [1]), W. ABNEY [2]), K. SCHAUM and V. BELLACH [3]), R. NEUHAUS [4]), and W. SCHEFFER [5]), the differences in density which appear in a photographic plate after exposure and development, may be ascribed to differences in the depth of the reduced silver haloid. So the image must have a

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1) Phot. Archiv. 1881; S. 85 u. 119.

  Phot. Mitt. Bd. 18; S. 65, 98 u. 235.

  J M. EDER, Handb d. Phot. 1902; Bd. III, S. 106 u. 108.

2) J. M. EDER, Hand. d. Phot. 1902; Bd. III; S. 102.

3) Phys. Zeitsch. 1902; Bd. IV; S. 4.

  J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 819.

4) Wied. Annal. d. Phys. u. Chem. 1898; Bd. 65; S. 164.

5) Phot. Chronik. 1904; S. 366.

  Phot. Rundschau. 1904; S. 121.

plastic shape similar to that formed by the pigment-gelatine printing process, the insoluble part being a normal copy, the soluble part a polarized one (monochrome pinatypy).

It is characteristic of the normal copy, if exposed and developed normally that the portions where the density is greatest show a duller surface when seen by light reflected at an angle than the clearest portions. This is to be attributed to the presence of reduced silver-haloid grains immediately under the free surface.

If the image lies against the free surface, it may be called a surface image, in opposition to a "depth" image, with which this is not the case.

The cause of the appearance of the surface image has been ascribed by P. H. EYKMAN and myself[1]) to the surface tension of the wet gelatine. So a silver-haloid gelatine layer may be looked upon as consisting of a series of layers, of which the top one, i.e. the one at the free surface, is the most sensitive, while every succeeding one lying under it, is less sensitive. The exposure required to render a beginning of reduction by the developer visible, the liminal value ("Schwellenwert") consequently seems to increase in proportion to the depth; that of the topmost layer is equal to the liminal value of the plate itself. We will call this the "absolute", that of the succeeding layers the "relative" liminal value.

Leaving aside, for clearnes's sake, the mutual differences in sensitiveness of silver-haloid grains in one single layer, to which J. M. EDER[2]) and J. PLENER[3]) have drawn attention, the differences in size and shape and the topographic situation of the grains, the normal copy may be represented as is shown in cross section and graphically in fig. 1.

The shape of the image of a polarized copy might be represented as indicated in fig. 2. I have found that this explanation cannot be applied to a single photographic image, but it is applicable to chemigraphic processes, catatypy and the silver-pigmentgum process.

In the case of some polarized copies, as the counter-positive and -negative, a normal copy is developed first, the reduced silver haloid of which is dissolved and, after a diffused exposure, redeveloped. Now a depth image originates (fig. 3). Owing to the diffused exposure the base of it, leaving aside slight differences in light absorption, will everywhere be about equally distant from the free surface.

[1]) Drude. Annal. d. Phys. 1907; Bd. 22; S. 119.
[2]) J. M. EDER, Handb. d. Phot. 1902; Bd. III; S. 64.
   Phot. News. 1883; p. 81.
[3]) Phot. Korresp. 1882; S. 306.

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According to the investigations of E. Englɪsh [1] and J. M. Eder [2] there are two images in the case of solarization. This question has not yet been satisfactorily cleared up, and a certain amount of confusion prevails as to the distribution of the normal and the polarized copy.

If the time of exposure, resp. the light intensity is increased, the reducibleness of the silver haloid increases in depth, finally to such a degree that provided the time of development be sufficient, the reduction extends to the glass, as is shown by the excellent microscopic preparations of W. Scheffer [3]. If solarization sets in, it will first occur in the apparently most sensitive layers, i. e. those at the free surface; consequently the reducibleness decreases from there, and on the time of exposure, resp. the intensity of the light being increased, it constantly extends further down. Thus an image is obtained as is graphically shown by fig. 4, from which it is at once apparent *that the solarized image is a normal copy and a surface image.* Under this image there is a polarized copy of greater density with *AB* for its base and from there to the glass there is a strip of fog, the density of which depends on the thickness of the emulsion.

That after all, in the case of solarization, the copy appears polarized, is therefore owing to the normal copy being of less density than the polarized one. It will, however, more or less reduce the contrasts and the wealth of detail. *It is consequently contrary to fact to understand polarization by solarization, as is always done.*

(In the figure the section of the solarized image is indicated by finer granulation, which is meant to show that the density has been reduced in that portion).

This at once accounts for the phenomenon occurring in the case of solarization of silver iodide gelatine discovered by Lüppo-Cramer [4]

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[1] Phys. Zeitschr. 1900; Bd. 2; S. 62.

J. M. Eder, Jahrb. f. Phot. u. Repr. 1902; S. 79.

Archiv. f. wiss. Phot. 1900; Bd. II; S. 260.

[2] Zeitschr. f. wiss. Phot. 1905; Bd. II; S. 340.

J. M. Eder, Handb. d. Phot. 1906; Bd. I; T. 2; S. 287.

Sitzungsber. d. Kaiserl. Akad. d. Wiss. zu Wien. Mathem-Naturw. Klasse; Bd. CXIV; Abt. IIa; Juli 1905.

[3] J. M. Eder, Jahrb. f. Phot. u. Repr. 1907; S. 31.

[4] I cannot omit quoting this experiment, which so clearly confirms the above :

"Eine auffallende Erscheinung beobachtete ich endlich noch bei einem *Solarisie-*"*rungsversuch* mit Jodsilbergelatine. Unter einem Negativ ergaben die Platten in "drei Sekunden bei diffusem Tageslicht ein ausexponiertes Bild. Eine sechs Stunden 'lang unter demselben Negativ belichtete Platte schien sich in Amidolpottasche, "in welcher sie neben der drei Sekunden belichteten Platte entwickelt wurde, zuerst

and which points to the very rapid decrease in reducibleness of silver iodide when solarized.

II. *A few phenomena occurring with solarization accounted for by considering the form of the image.*

From the form of the image in fig. 4 it appears how impregnation of the silver-haloid gelatine plate with bichromate before exposure may influence the result obtained, which was pointed out by BOLAS [1]). J. M. EDER and G. PIZZIGHELLI [2]) attributed the result exclusively to hardening of the gelatine, by which development in the normal image is disturbed, and in which solarization acts hardly any part. It is evident that this image in the hardened gelatine more or less coalesced with the solarized image, in proportion to the strength of the bichromate solution employed, by which the development of the latter is suppressed to a greater extent and the polarized copy appears richer in contrast and detail. The fog, however, is not done away with.

While in the case of normal copies the latter may be removed with FARMER's reducer [3]), this treatment does not succeed in the case of polarization. The slight diffusion of this reducer discovered by W. SCHEFFER [4]), by which the action slowly progresses downwards from layer to layer, at once accounts for this phenomenon.

Of more significance to our knowledge of the latent image is the so-called neutralization of solarization by retarded development. That the said phenomenon is regarded as such is only attributable to the ideas of solarization and of polarization being confounded.

Development is retarded either by decreasing the amount of alkali

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"gar nicht zu reduzieren, während das kurz exponierte schon in allen Einzelheiten "erschienen war. Nach einiger Zeit merkt man indes, dass auch auf der überbe- "lichteten Platte ein Bild vorhanden ist, dasselbe sitzt nur in den *tieferen Schichten* "allerdings als normales Diapositiv, d. h. noch nicht solarisiert während in der "Aufsicht erst nach längerer Entwicklung etwas zu sehen ist. Beim Fixieren merkt "man deutlich, dass *in der obersten Schicht* der lange belichteten Platte kein Bild "vorhanden ist, indem nach kurzem Fixieren das Bild auch in der Aufsicht kräf- "tiger wird, offenbar weil das unreduzierte Jodsilber der obersten Schicht wegge- "nommen wird". (J. M. EDER, Jahrb. f. Phot. u. Repr. 1903; S. 46. Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17).

[1]) J. M. EDER. Handb. d. Phot. 1902; Bd. III; S. 115.
    Phot. News. 1880; Vol. 24; p. 304.
[2]) J. M. EDER. Handb. d. Phot. 1902. Bd. III; S. 115.
[3]) J. M. EDER. Handb. d. Phot. 1902 Bd. III; S. 555.
[4]) Brit. Journ. of Phot. 1906; p. 964.
    J. M. EDER. Jahrb. f. Phot. u. Repr. 1907; S. 26.

in the developer or by the addition of potassium bromide. That only the rapidity of reaction of the developer is reduced, I was able to ascertain by the so-called neutralisation of solarization with a developer (rodinal 1 in 10) at a lower temperature. First a normal copy is developed, which when development is continued, turns into a polarized one.

However, the normal copy obtained in this way, differs very much from an ordinary one. When viewed by light reflected at an angle, it is just in the densest portions that the surface is found to have the highest gloss; consequently here the grains do not lie against the surface. After the copy has changed into a polarized one, in which the polarized depth image predominates, the surface remains unchanged, and now shows the highest gloss in the clear portions. Consequently the surface image has not undergone a reversion of density proportions, from which it follows *that the normal copy obtained by retarded development must be the solarized image*[1]). *This cannot be ascribed to a change of the solarization, i.e. to a change in the substance of the solarized latent image.*

Consequently in the surface glass we have a means of ascertaining in the case of solarization, whether an agent reacts upon the substance of the latent image or upon the development. Thus I could ascertain *inter alia*, that chromic acid mentioned by J. M. EDER [2]) and ammonium persulphate referred to by K. SCHAUM and W. BRAUM, which both exercise a hardening influence upon the gelatine, at the same time also react upon the substance of the latent image in the case of solarization, by which it is reduced to the substance of the ordinary latent image.

III. SABATIER's *polarization*.

If during the development of a plate light is admitted, three different phenomena may occur:

1. If a very slight amount of light is admitted, the plate in the developer shows an increase of reducibleness.

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1) It stands to reason that during the appearance of the normal copy in the developer, consequently before polarization sets in, development of the non-solarized silver haloid in the lower layers may take place. Consequently it is better to say that the solarized image is only formed within a certain definite time of development.

2) Phot. Korresp. 1902; S. 647.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 23.

J. M. EDER. u. E. VALENTA. Beiträge zur Photochemie. 1904; II; S. 168.

J. M. EDER. Handb. d. Phot. 1903. Bd. III; S. 828.

3) Phot. Mitt. 1902; S. 224.

2. If more light is admitted the image partly disappears, and a more or less fogged plate is obtained with partly a normal and partly a polarized copy, which shows great resistance to further development.

3. If still more light is admitted, the copy is polarized.

This last phenomenon I call SABATIER's polarization.

J. M. EDER [1]) credits SABATIER with first observing it, and says that SEELY gave the following explanation of it: The beginning of the development takes place at the surface; by the secondary exposure this developing image is copied upon the silver haloid underneath it, and as this exposure is more powerful than the first, the second image also develops more strongly, and total polarization results.

From the experiments carried out by me it appeared that the secondary exposure stopped the development of the surface image, for by reflected light it was seen that it did not increase in density any more, while total development of the whole surface might be expected. In order to ascertain to what extent the copying action of the developing surface image is operative in polarization, I effected the secondary exposure, at the advice of P. H. EYKMAN, on the glass side of the plate.

The exposed plate was developed for a short time, and just after the appearance of the image it was, while still in the developer, covered with a piece of opaque, black paper, which was everywhere pressed tightly against the emulsion to prevent the formation of air-bells, from which uneven development might arise, and then the glass side was exposed to direct daylight. As the quantity of developer soaked up by the paper was small and the temperature was below the normal one, the plate, to save time, was put in the developer again in the dark room, great care being taken to prevent light from reaching the front of the plate. After fixation a polarized copy appeared.

This shows that the copying of the developing image at most acts a very secondary part in the appearance of polarization.

The latter can only be ascribed to the further development of the surface image being stopped, and to the reducibleness of the silver haloid underneath it being increased. Consequently here again two images are formed, one under the other: at the top a normal copy of little density, and under it a polarized one of greater density, corresponding to that of the polarized copy in fig. 3 in the case of solarization.

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1) J. M. EDER Handb d. Phot. 1898; Bd. II; S. 82.

The similarity between SABATIER's polarization and solarization is so great, that R. LYLE[1]) attributed the phenomenon mentioned sub 2 to the first zero condition of JANSSEN's periodicities of solarization being reached[2]). In one of my experiments it appeared to me that this similarity only existed in so far as no image was to be observed. The first zero condition is characterised by the maximum of density obtainable, whilst the plate in question remained very thin. Consequently the cause of the disappearance of the image cannot lie in this.

By transmitted light, too, the plate does not show polarization in the portions exposed most intensively by the primary exposure, but in the portions that received the smallest amount of light. (Therefore SABATIER's polarization cannot be ascribed to solarization). It is easy to understand that the relative liminal value of a lower layer is first reached in those portions where the absorption of the surface image is the least, and where this layer, at the same time, is situated nearest to the free surface. So in this case the copying quality of the surface image exercises its influence.

IV. Herschel's effect.

By HERSCHEL's effect I understand polarization by double exposure. It differs from polarization by solarization in that much smaller amounts of light-energy are sufficient to produce it, and in the reducibleness of the primarily exposed silver haloid decreasing at once on a secondary exposure.

The duration of the primary exposure must always exceed the liminal value of the plate. After the secondary exposure has exceeded a certain maximum (the critical exposure), the plate shows a normal copy again. The value of the critical exposure depends entirely on the primary exposure. This has led to the so-called CLAYDEN's effect[3]) (black lightning) being looked upon as a new phenomenon of the photographic plate.

The first observation dates from 1839, and was made by J. HERSCHEL, who stated that the red and the yellow rays of the spectrum could

[1]) Phot. Centralbl. 1902, S. 146.

[2]) Compt. rend. 1880; T. 90; p. 1447. T. 91; p. 199.
Moniteur de la Phot. 1880; p. 114.
Beibl. z. d. Annal. d. Phys. u. Chem 1880; S. 615.
J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 306 1898, Bd. II; S. 78.
J. M. EDER, Jahrb. f. Phot. u. Repr. 1894; S. 378.

[3]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1901; S. 610.
Camera Obscura. 1901; bldz. 513.
J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 312.
„   „   „   „   1903; Bd. III; S. 834.

destroy the latent image of the blue and violet ones. At the same time a change in the degree of colour sensitiveness was ascertained. This was confirmed by CLAUDET [1]), H. W. VOGEL [2]), W. ABNEY [3]), P. VILLARD [4]) and R. W. WOOD [5]). E. ENGLISCH [6]), H. W. VOGEL and W. ABNEY, however, considered this phenomenon to be solarization. An experiment published by P. VILLARD clearly shows that in the case of very advanced exposures the critical exposure does not appear any more, and the whole phenomenon coalesces with solarization. The highest sensitiveness of the plate is manifested towards red, the lowest to green.

WARNERKE [7]) observed HERSCHEL's effect in images obtained by printing, and P. VILLARD, R. W. WOOD, R. LUTHER and W. A. USCHKOFF [8]) with Rontgen rays in the case of primary exposure. At the same time they demonstrated that the phenomenon did not appear if these exposures were reversed.

J. STERRY [9]) communicated another variety, viz. that certain kinds of chemical fog can be neutralized by weak light.

Some time ago one of my friends showed me a few camera exposures on EASTMAN films [10]), which I recognized as the phenomenon observed by J. STERRY. They had been exposed once, but had been in the camera for about 3 years without any precautions having been taken except that light had been prevented from reaching them. Consequently in this case the diffused exposure had been replaced by a chemical process of analysis, which had acted similarly, and had been exercised upon the silver bromide by the vapours given off by the celluloid, which had been diffused in the silver bromide gelatine.

Fig. 5 is an outdoor subject; it had a short exposure and shows various abnormalities. Nearly the whole copy is polarized, with the exception of the sky near a, where the critical exposure had been exceeded. The dogs in the foreground, reflecting the greatest amount of light there, show the beginning of the formation of a normal copy,

[1]) Annal. d. Chimie et de Phys. 1848; 3e série; T. XXII.
[2]) H. W. VOGEL. Handb. d Phot. 1890|; Bd. I; S. 221.
[3]) Phot. Archiv. 1881; S. 120.
[4]) Soc. d'encourag. pour l'Industrie nation. Extr. d. Bulletin; Nov. 1899.
[5]) Astrophys. Journ. 1903; Vol. XVII; p. 361.
[6]) J. M. EDER. Jahrb f. Phot. u. Repr. 1902; S. 73.
[7]) Phot. Arch. 1881; S. 120.
[8]) Phys. Zeitschr. 1903; S. 866.
[9]) This paper I only know from a resumé in J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 425.
[10]) The lens of the camera was a slow aplanat, and was used with full opening for the interior; for the outdoor exposure it was stopped down.

and so do the shoulders of the female figure to the right, owing to which especially the left shoulder shows a false relief. Consequently the critical exposure is reached after the greatest transparency of the image has been obtained.

Between these beginnings of a normal copy and the polarized copy there is a clear strip, which is narrower where the exposure has been stronger. The dog to the left shows greater density of the normal copy than the one to the right, where the bright strip is broader. This strip occurs in the brighter parts in a manner that is the exact opposite of the way it occurs round the outlines of the leaves of the tree and of the bare trunk in the background; a few shoots are even quite white. Here the strips are found in the darkest parts, and decrease in width towards the right of the tree top, round which a smaller light intensity has been active.

The wall was more strongly lighted to the left than to the right, and appears slightly darker there, but still it remains polarized, which is easier to see in the original film than in the reproduction. The left side of the tree top shows more halation than the right, while no halation whatever is to be seen in the part of the sky near a, which was subject to the action of light with greater contrasts. Here, however, one would have expected that halation would have acted in the opposite direction, viz. not decreasing in density in the darkest portions, but increasing in the lighter ones.

The comparatively slight density of the sky near a is striking, and so is the low colour sensitiveness to green (grass and foliage), while the dark blond and dark brown hair of the two female figures show a stronger action of the light, which can be seen better in the original copy. The wall in the background is white, so that here the colour sensitiveness to the red of the bricks cannot be ascertained

Fig. 6 renders the critical exposure still more strikingly. It represents an interior; the film was exposed a few seconds, and shows every object in the room polarized, even a large portion of the halation owing to the light from the left window. What is seen outside through the windows has been copied normally; here, consequently the critical exposure has been exceeded. The halation has partly made the lead setting of the coloured glass appear normal again, while to another portion it has given greater density owing to the action of the light being stronger. A large part of the right half and a smaller part of the left bottom section show differences in density, which must be ascribed to uneven action of the chemical reactions during the time the film was kept. Fig. 5 also shows this, but in a slighter degree; here, however, it is less noticeable on account of the wealth

of detail of the image. The action being slighter to the right, the images are seen to be thinner accordingly.

The same thing is to be observed in a Röntgenogram placed at my disposal by P. H. EYKMAN. The plate was exposed to Röntgen rays with a so-called intensification screen (calcium wolframate screen), and laid aside some time before development. Calcium wolframate postluminesces [1] owing to which a plate is consequently further exposed. The objects photographed with Röntgen rays were a piece of bone, a piece of thin and a piece of thicker, insulated copper wire. Fig. 7 gives a reproduction of the negative. The places of the thin copper wire show development of the silver bromide which is nearly as strong as in the field, where the Röntgen rays and the luminescence together have acted most strongly. .A narrow strip along the edge indicates how far the screen covered the plate ; consequently there only the R. rays have acted. The place of the thin copper wire does not show a trace of development there ; consequently the exposure remained below the liminal value.

The development of this place cannot be put down to irradiation through the screen ; in that case the same thing would have to be observed in the case of the thick copper wire and the edge of the screen. Consequently the R rays must really have acted in such a way in that place, that the screen luminesced and this acted upon the silver bromide, while the exposure to R. rays remained below the liminal value.

P. H. EYKMAN also showed me a negative in the case of which the screen after irradiation had only been brought into contact with an unexposed plate [2]. It showed a very thin image, from which it follows that the strongest action of the screen takes place immediately after the transformation of the absorbed Röntgen energy. Consequently if in the case of a röntgenogram with a calcium wolframate screen the action of the R. rays could be prevented, much shorter exposures would be sufficient to produce a good image. Hitherto this has proved to be impossible.

Another fact important for our knowledge of the latent image may be gathered from fig 6. The right bottom corner shows that the thinner the fog of diffused exposure becomes, the thinner also the polarized copy is. From this it follows *that in the case of secondary exposure the liminal value is lower than in the case of primary exposure, i.e. the amount of light necessary to effect the begin-*

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[1] Fortschr. a. d. Geb. d. R-Str. 1901; Bd. IV; S. 180.

[2] The calcium wolframate screen was exposed to the R rays at the same time as the negative of Fig. 7.

*ning of a decrease in reducibleness is smaller than is necessary for
a beginning of an increase of this power with the original condition
of the silver bromide.*

V. *The theory of the latent image.*

In the case of the theory of the latent image two facts have to
be observed, which are directly connected with each other:

1. The action of the light upon the silver haloids;

2. The physical or the physical and chemical changes in the silver
haloid resulting from this action.

The theory proper of the latent image is only restricted to the
latter, consequently comprises only secondary phenomena. Of all
the theories enunciated, only the subhaloid theory of CHOISELAT and
RATEL [1]) has maintained itself, especially owing to the subsequent
investigations of M. CAREY LEA [2]), H. WEISS [3]), J. M. EDER [4]), and
others. While J. M. EDER [5]) looks upon silver subhaloid as a
molecular compound, M. CAREY LEA [6]), E. BAUER [7]), L. GUNTHER [8]),
and LUPPO-CRAMER [9]), consider it an absorption compound of colloidal
silver and silver haloid, thus practically maintaining ARAGO's old
silver-germ theory in a new shape. However, it is impossible yet to
point out a single fact in photography from which it appears which
of these two theories is to be preferred; all chemical reactions on
the latent image might be accounted for by either theory and

[1]) Compt. rend. 1843: T. 16; Nr. 25.
   „   „   .,   T. 17; Nr. 4.
  J. M. EDER. Handb. d. Phot. 1898; Bd. II; S. 111.

[2]) Americ. Journ of Science. 1887; Vol. 33; p. 349.
  Phot. Korresp. 1887; S. 287, 344 u. 371.

[3]) Zeitschr. f. phys. Chemie 1905; Bd. 54; S. 305.
  Chem. Centralbl. 1906; Bd. I; S. 807.
  J. M. EDER. Jahrb. f. Phot. u. Repr. 1906; S. 473.

[4]) Sitzungsber. d kaiserl. Akad. d Wiss. zu Wien. Mathem.-naturw. Klasse.
  Bd. CXIV; Abt. IIa; Juli 1905.
  Zeitschr. f. wiss. Phot 1905; Bd III; S. 329.
  J. M. EDER. Handb d. Phot. 1906; Bd. I; T. 2; S. 277.
  Phot. Korresp. 1905; S. 425 u. 476.
   „   „   1906; S. 81, 134, 181 u. 231.
   „   „   1907; S. 79.

[5]) See note 4.

[6]) See note 2.

[7]) Zeitschr. f. phys. Chemie. Bd. 45; S. 618.

[8]) Abhand. d. naturk. Ges. Nürnberg. 1904; Bd. 15; S. 26.

[9]) Phot. Korresp. 1906 u. 1907.
  LUPPO CRAMER. Photogr. Probleme. 1907; S. 193.

neither of them has hitherto afforded a definite explanation of the various photographic phenomena.

As the photo-chemical process of analysis upon the silver haloid is only characterized by a continuous reduction process, it is quite natural to assume this also in the cases of the solarized latent image Still there are a few phenomena which seem to contradict this.

Thus W. ABNEY [1]) assumed the formation of an oxybromide, and founded this assumption on the fact observed that potassium bichromate and potassium permanganate, perhydrol and a few anorganic acids promote solarization. The anti-solarizing action, also pointed out by him, of reducing agents, like pyrogallol, ferrous sulphate, ferrocyanide of potasium, nitrites, and sulphites, has only been judged from the appearance or non-appearance of polarization, and may be entirely reduced to retarded development.

LÜPPO - CRAMER [2]) considers the oxidation theory of solarization absurd. He points to the solarization of the plate even if no oxygen is admitted, and to the circumstance that all the agents that prevent solarization, are - halogen-absorbing substances. As a characteristic example he mentions silver nitrate, the anti-solarizing action of which is, according to him, to be ascribed to halogen-absorption, not to oxidation, and considers this action analogous to that of nitrites, sulphites and hydroquinone.

This view is at variance with his criticism of the oxidation theory, in which he also points to the continuous loss of halogen in the case of continued exposure of the silver haloid, and to his observation that a bromide solution counteracts solarization, and may even entirely neutralize the latent image [3]). *Consequently halogen-absorption must promote solarization.* The promotion of solarization mentioned by W. ABNEY, and referred to above is not to be ascribed to oxidation, but to halogen absorption.

That oxidation of the substance of the latent image neutralizes solarization, has been ascertained by J. M. EDER [4]) with his chromic acid reaction, and by K. SCHAUM and W. BRAUN [5]) with their ammonium persulphate reaction. That in this case we really have not the

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[1]) Proc. Roy. Soc. 1873; Vol. 27; p. 291 a. 451.

[2]) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 138.

[3]) J. M. EDER, Jahrb. f. Phot. u. Repr. 1902; S. 481.

[4]) Phot. Korresp. 1902 S. 647.
   J. M. EDER, Jahrb. f Phot. u. Repr. 1903; S. 23.
   J. M. EDER, u. E. VALENTA, Beiträge zur Photochemie. 1904; II; S. 618.
   J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 828.

[5]) Phot. Mitt. 1902; S. 224.

phenomenon of retarded development I could observe through the formation of a dull surface image. Further Luppo-Cramer[1]) proved that the silver subhaloid of Poitevin's photochromics undergoes regression to silver haloid by oxidation. J. M. Eder[2]) described the same thing in his investigations of the latent image with the nitric acid reaction.

Quite a different view of the progressive photochemical analysis of silver haloids, was given by H. Luggin[3]). He stated that in the case of more intensive exposure, also a proportionately greater amount of formed silver haloid, under the influence of the increasing halogen pressure takes from the silver haloid the power of affording germ-points for the deposit of metal, and that consequently halogen-absorbents (chemical sensitizers) would be the best means of keeping the halogen pressure as low as possible, and so of preventing solarization. Consequently he considers solarization as a phenomenon consisting in the prevention of germ-formation. His statement: "The beginning of solarization may often be obviated by selecting smaller stops and increasing the exposure accordingly," is confirmed in the case of silver iodide gelatine[4]).

Still this proposition that halogen absorption prevents solarization is at variance with what goes before. I have therefore investigated this matter more closely.

Silver haloid is decomposed by the action of light, but a polished silver bar exposed in the light to halogen vapours, at once combines with it to form halogen silver. Consequently in the presence of an excess of halogen the silver haloid is not decomposed.

A highly sensitive silver bromide gelatine plate, which was partly coated with collodion, was exposed to direct daylight. It was observed that the photo-chemical decomposition under the collodion remained considerably behind that of the free surface, and had not even increased appreciably after an exposure of several weeks. The violet brown discolouration appeared only at the free surface, and could be removed by the plate being rubbed carefully. A plate, exposed at the same time on the glass side, also showed retardation as to the photo-chemical decomposition process, and against the glass the silver bromide seemingly remained unaltered. Consequently the fact that halogen prevents diffusion counteracts decomposition. In the case of

[1]) Phot. Korresp. 1907; S. 439.
[2]) See note 4, p.
[3]) J. M. Eder, Jahrb. f. Phot. u. Repr. 1898; S. 162.
[4]) J. M. Eder, Handb. d. Phot. 1906. Bd. I; T. 2; S. 309.
   Luppo-Cramer, Phot. Probleme. 1907; S 152.

an excess of liberated halogen the opposite reaction takes place, which is quite in accordance with the regression of the latent image by a bromide solution in the case of silver bromide, as found by LUPPO-CRAMER.

The diffusion of liberated halogen will always take place in a smaller degree in the series chlorine, bromine, iodine, on account of the atomic weight rising.

H. LUGGIN's rule must, therefore, be modified to the effect that in the case of a certain definite light intensity the progressive and regressive reduction get into a condition of equilibrium, which is only got over by a loss of halogen (absorption by the chemical sensitizer and diffusion).

The same thing was said in other words before now by J. PRECHT [1]), but on the ground of the appearance of solarization.

With this modified proposition of H. LUGGIN the deviations [2]) from R BUNSEN's and H. ROSCOE's reciprocity rule [3]) can be accounted for, to which also belong the phenomena in the case of silver iodide gelatine just mentioned.

The knowledge of the latent image is arrived at by development. While the exposure causes decomposition of the silver haloid accompanied by a quantitative increase in silver subhaloid, a decrease of reducibleness appears during development after a certain maximum of exposure. The solarization phenomenon is, therefore, a development phenomenon in the sense that development, owing to the modified properties of the latent image, shows a change.

Consequently in order to account for solarization a knowledge of the nature of development is requisite. Without it solarization remains an unsolvable problem.

Two methods of development are distinguished: The physical and the chemical method [4]). Physical development is characterized by a deposit of a reduced silver compound from the developer on the exposed silver haloid; chemical development by reduction of the exposed silver halogen itself.

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[1]) Zeitschr. f. wiss. Phot. 1905. Bd. III; S. 75.
[2]) J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 48 u. 49.
       „   „ „ „ 1902; Bd. III; S. 228.
       „   „ „ „ 1898; Bd. II; S. 3 u. 5.
    Phot. Mitt. 1890; S. 261.
    Proc. Roy. Soc. 1893; Vol. 54; p. 143.
[3]) POGGENDORF Annal. d. Phys. 1862, Bd. 117; S. 538.
[4]) J. M. EDER, Handb. d. Phot. 1898; Bd. II; S. 29.
     „   „   „   „ 1906; Bd. I; T. 2; S. 250.

By W. OstwaLD [1]), K. Schaum and W. Braun [2]) it was supposed that the reduction of the silver bromide with chemical development was in the first instance brought about by a minimum amount of silver bromide dissolving as positive silver- and negative haloid-ion, after which the reduced substance was precipitated upon the germs. Lüppo-Cramer [3]) succeeded in showing that a number of developing processes which were formerly looked upon as being purely chemical in their nature, not only in reality proceed physically, but that every chemical development is also partly of a physical character. W. Scheffer [4]) was the first to show by a microscopical investigation that the entire chemical development is physical in its nature, i.e. it is brought about by molecular attraction between the photo-chemically reduced silver haloid, the germ, and the reduced feeding-substance. This, consequently, accounts for the altered structure of the exposed silver bromide gelatine plate before and after development [5]).

Still the development of the photographic plate by the so-called chemical method really shows a difference from the physical method. Lüppo-Cramer [6]) succeeded in demonstrating that the substance of the image in the case of a negative developed by the so-called chemical method, still contained bromine by the side of ordinary silver, which bromine he supposed to be a constant solution of silver in silver bromide. From this he infers that during the development, beside the silver another intermediate product must originate. It is only natural to assume, on the analogy of the reduction process of the silver haloid to silver through subhaloid, that also in the case of so-called chemical development the reduction takes place in the same way. Thus it appears that between chemical and physical development there is only this difference that the former keeps the subhaloid in solution with more difficulty than the latter, owing to which perfect reduction cannot take place. This at the same time accounts

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[1]) W. Ostwald. Lehrb. d. allgem. Chemie. 1893; Bd. 2; S. 1078

[2]) J. M. Eder. Jahrb. f. Fhot. u. Repr. 1902; S. 476.
Phot. Mitt. 1902; S. 229.

[3]) Lüppo-Cramer. Phot. Probleme 1907. S. 159.

[4]) Phot. Rundschau 1907; S. 142.
Phot. Korresp. 1907; S. 384.

[5]). S. E. Sheppard and C. E. K. Mees. (Zeitsch. f. wiss. Phot. 1905; Bd. III; S. 355) consider V. Bellach's observation that the size of the grain of the developed image decreases during the drying of the emulsion, to be in accordance with G. Quincke's foam-structure theory of the silver haloid grains which, according to him, contain gelatine. The non-coalescence of the exposed with the developed grain shows the incorrectness of this view.

[6]) Phot. Korresp. 1905 S 319.

for the fact that the image developed with certain developers loses density in the fixing bath; this loss of density is analogous to what is observed in the case of P. O. P. papers with silver chloride.

This further explains another apparent contradiction. While with silver chloride a lower and with silver bromide a higher degree of sensitiveness to light is observed, in other words, while quantitatively the same photochemic decomposition of silver bromide takes place with less absorption of light energy than in the case of silver chloride the exact opposite is seen to take place with the increase in density during development, which has been pointed out by H. and R. E. LIESEGANG [1]), KÖNIG [2]) and LÜPPO-CRAMER [3]). Considering that silver chloride possesses a higher solubility, resp. has the power of bringing a greater number of ions into solution than silver bromide, it is easy to understand that quantitatively reduction can take place in a larger measure per unit of time, notwithstanding silver chloride is a more constant compound than silver bromide.

With silver iodide the same thing is observed still better. The reducibleness, resp. solubility is still less in this case, which has often occasioned the unjustified conclusion, that silver iodide is less sensitive to light than silver bromide, while the exact opposite is observed in the case of daguerreotypy and the wet collodion process, since here the feeding substance for development is introduced from without. Accordingly LÜPPO-CRAMER could use with silver iodide developers like amidol potassium carbonate, triamidophenol, diamidoresorcin, and triamidoresorcin, which show a far too great rapidity of reaction for silver bromide plates.

The higher sensitiveness of silver iodide-bromide plates as compared with silver bromide plates, owing to which more detail can be obtained in the darkest parts of the image, may therefore be ascribed to the more rapid formation of germs in the case of silver iodide, while the silver bromide serves as feeding substance for the developer. This further appears from the optical sensitizing of silver iodide-bromide plates.

While silver bromide can easily be made colour sensitive, this is not the case with silver iodide, which has been pointed out by J. M. EDER [4]), LÜPPO-CRAMER [5]), and others. Still both may be dyed

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[1]) Phot. Mitt. 1901; S. 362.
   Phot. Wochenbl. 1901; S. 405.
   J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 572.
[2]) Phot. Korresp. 1903; S. 14.
[3]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 401.
[4]) J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 269.
[5]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 46.
                                        „   „   „   1904; S. 390.
   Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17.

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by optical sensitizers, but in this case the silver iodide-bromide plate behaves more like a silver iodide plate.

At the 79th German Physical and Medical Congress held in Dresden in 1907 W. Scheffer[1]) communicated a solarization theory founded upon his microscopic investigations[2]), which explains solarization in quite a simple way.

When the exposed silver bromide gelatine plate is being developed certain grains ("Ausgangskörner") send out germs, upon which the reduced substance is deposited, because other grains ("Nahrkörner", formerly called "Lösungskörner") are dissolved in the developer and cause the growth of the germs. In an overexposed emulsion too many germ-producing grains "explode", and an insufficient number of "feeding" grains remain, so that no image of sufficient density can be formed. Consequently this theory is founded upon the transition of "feeding" grains into germ-producing ones by exposure, or rather of silver haloid into silver subhaloid.

This theory cannot be reconciled to the fact found by J. Sterry[3]), J. M. Eder[4]) and Lüppo-Cramer[5]), that solarization can also appear with primary fixation, for in this case the feeding substance is supplied from without. The same holds good with regard to daguerreotypy.

B. Homolka's solarization theory[6]) : "In the decrease of the amount of silver bromide I recognize the primary cause of solarization", is irreconcilable to the above, not to mention the circumstance that these two theories cannot explain the second reversion of solarization, and cannot account for the fact that even with the strongest overexposures an excess of silver haloid, i. e. of feeding substance, can be proved to be still present in the emulsion.

From the solarization with primary fixation it therefore appears, that the silver haloid germ loses this germinating property on further exposure, i. e. through the continued photochemical decomposition it has passed into another subhaloid containing less halogen, which possesses no germinative property. O. Wiener[7]) proved the possibility of the existence of more subhaloids. Let us call the first the α-silver subhaloid and the second the β-silver subhaloid.

[1]) Phot. Korresp. 1907; S. 487.

[2]) Phot. Rundschau. 1907 ; S. 65 u. 142.
   Phot. Korresp. 1907. S. 233 u 384.

[3]). J. M. Eder. Jahrb. f. Phot. u. Repr. 1899; S. 289.

[4]) J. M. Eder. Handb. d. Phot. 1906; Bd. I; T. 2; S. 312.

[5]) Lüppo-Cramer. Phot. Probleme, 1907; S. 150.

[6]) Phot. Korresp, 1907; S. 168.

[7]) J. M. Eder. Jahrb. f. Phot. u. Repr. 1896; S. 55.

The reappearance of reducibleness in the case of continued exposure, the so-called second reversion of solarization might then again be attributed to a newly formed γ-silver subhaloid, or, as the third reversion has not been observed, to a metallic silver germ or what is also possible, to both.

It must be emphasized at the very outset, that it is by no means impossible that before the α-silver subhaloid one or more other sub-haloids, richer in halogen, are formed, which possess no germinative property, for a primary exposure below the liminal value of the plate points to photochemical decompositions taking place through the occurrence of auto-sensitizing [1]), so that the liminal value cannot be considered identical with the photochemical induction. Nor must it be inferred from the above that the α- or the β-silver subhaloid does not consist of more than one silver subhaloid.

Consequently it appears from all this that sensitiveness to light and reducibleness must on no account be identified, as is generally done.

The untenableness of the existing theories of HERSCHEL's effect by CLAUDET, P. VILLARD, R. W. WOOD and WARNERKE is accounted for by this faulty identification of reducibleness with sensitiveness.

For the appearance of HERSCHEL's effect it is necessary that the primary exposure should exceed the liminal value of the plate. Con-sequently α-silver subhaloid must have been formed.

That by the secondary exposure a regressive reaction occurs between the α-silver subhaloid and halogen, cannot be assumed, because in the case of prolonged exposures HERSCHEL's effect coalesces with solarization, in connection with which the formation of the β-silver subhaloid without germinative property has already been stated. The experiments of W. ABNEY mentioned above, also prove that halogen absorption promotes the phenomenon. Consequently the secondary exposure acts in such a way that the α-silver sub-haloid formed photochemically by the first exposure is reduced to β-silver subhaloid more rapidly than it has been possible for *an equal quantity* of α-silver subhaloid to be formed afresh. (In this case it may happen that the silver subhaloid has already entirely been photochemically dissolved, before the silver haloid has been able to supply it). This appears from the discussion of fig. 6. The photochemical induction of the α-silver subhaloid is, therefore, lower

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[1]) Vide: J. M. EDER. System der Sensitometrie phot. Platten. Sitzungsber. d. kais. Akad. d. Wiss. in Wien 1899; IIa; Bd. 108; S. 1407. J. M. EDER u. E VALENTA. Beiträge z. Photochemie. 1904; Bd. II; S. 48.

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than the liminal value of the silver haloid. *Consequently the α-silver subhaloid is a substance of greater sensitiveness to light than the silver haloid.*

If with the secondary exposure the amount of α silver subhaloid originally present is exceeded, a normal copy is obtained again. The critical exposure, therefore, is that secondary exposure by which the same amount of α silver subhaloid is formed as was present after the primary exposure. So the best gradation of the polarized copy in the case of HERSCHEL's effect is obtained, if lower light intensities are employed, as is shown by experiments.

The amended proposition of H. LUGGIN states that with a certain definite light intensity the progressive and the regressive reaction in the silver haloid arrive at a state of equilibrium, if the liberated halogen is not removed. This removal of halogen, either by diffusion or by chemical sensitizers, is therefore of paramount influence upon the origination of HERSCHEL's effect. Consequently the most successful experiment is obtained with an emulsion which immediately absorbs the liberated halogen, or what is better even, if between the primary and the secondary exposure the plate is put aside for a considerable time, by which the liberated halogen is diffused out of the emulsion. It is still simpler to treat the plate after the primary exposure with a halogen absorbent, as was done by W. ABNEY, and we therefore regard judson blue, mentioned by H. W. VOGEL[1]) as a substance probably behaving analogously.

Therefore the direct decomposition of the silver haloid by reducers as in the case of J. SERRY's experiments and fig. 5 and 6, in which the liberated halogen enters into combination, acts so favourably upon HERSCHEL's effect.

This makes P. VILLARD's statement clear that not all emulsions are equally suitable for experiment, as in the various emulsions there are different chemical sensitizers (both in quality and in quantity).

At the same time the nature of the phenomena in the case of intermittent exposure becomes clearer now.

That the effect of development upon silver bromide gelatine (but not necessarily the photochemical decomposition) is always slightly less than with a continuous exposure of the same duration was observed by W. ABNEY[2]), K. SCHWARZSCHILD[3]), and others. Many

[1]) H. W. VOGEL. Handb. d. Phot. 1890; Bd. I; S. 221.

[2]) Photography 1893; p. 682.
   Phot. Archiv. 1893- S. 339.
   J. M. EDER. Jahrb. f. Phot. u. Repr. 1894; S. 373.

[3]) Phot. Korresp. 1899; S. 171.

beginners in photography have observed the same thing when having made two exposures of different objects on the same plate. In this case it is easy to observe that not the sum of the two images is obtained, but that in one place one object dominates, in another place the other object.

According to K. SCHWARZSCHILD the result in the case of the exposure being intermittent depends, *inter alia*, upon the relation between the interval and the duration of the separate exposures; the longer the interval the better opportunity the halogen has of escaping by diffusion, or of being absorbed by a chemical sensitizer, and the more readily the next exposure will photochemically decompose the α silver subhaloid germ, which is more sensitive to light than the silver haloid, into β silver subhaloid and halogen, owing to which the result of development, apart from the photochemical induction which is to be exceeded again, will remain below the sum of the components.

The difference in sensitiveness to light between silver haloid and the α silver subhaloid appears, according to the above experiments, to depend largely upon the kind of light with the seconday exposure. The less sensitive the silver haloid and the more sensitive the α silver subhaloid is to a given colour, the more pronounced Herschel's effect will be. The smaller this difference, the more rapidly the silver haloid will produce fresh α silver subhaloid germs; it is true, in this case polarization is observable, but the minimum reducibleness is soon reached. Further this is, of course, also dependent upon the amount of α silver subhaloid, i. e. upon the duration of the primary exposure. Perfect neutralization of reducibleness need not occur then.

Consequently the colour sensitiveness occurring in the case of HERSCHEL's effect is to be ascribed to the colour sensitiveness of the α silver subhaloid. Not one of the theories of the latent image enunciated hitherto can account for the phenomenon in such a simple way as the subhaloid theory. The subhaloids are dyes of quite different colours from silver haloid, and consequently with quite different spectra, owing to which the possibility exists of quite different colour sensitiveness, as in fact actually appears from the experiments of O. WIENER [2]).

P. VILLARD proved spectroscopically that the greatest difference between the liminal value of the silver haloid and the photochemical induction of the α-silver subhaloid is situated in the red

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[1]) Probably these photochemical decompositions proceed according to an exponential formula.

[2]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1896; S. 55.

and consequently that the α-silver subhaloid is a substance sensitive to red. If a silver bromide gelatine plate is exposed to the action of a continuous spectrum, the reducibleness in the case of increasing exposure will proceed from blue to red. While after development it is observed that with increased exposure the density of the plate increases about and in the spectral blue, the yellow, the orange, and especially the red obtain only very slight densities. Consequently it is evident that the cause why the density of the image in the red, yellow, and orange portions cannot increase above a maximum, which is very low, lies in the a silver subhaloid possessing a far greater sensitiveness to red than the silver haloid, so that very soon a state of equilibrium has been reached, in which in a progressive process as much α-silver subhaloid is formed as destroyed.

The substance of the developable latent image is considered identical with M. CAREY LEA's photohaloid. Now how does this behave in red light?

M. CAREY LEA [1]) exposed his pink photohaloid to the action of a spectrum ; while under all colours the photohaloid changed, it remained unchanged in the red. From this it appears that the subhaloid germ of the latent image must be another substance than M. CAREY LEA's photohaloid.

The behaviour of Röntgen rays differs from that of other kinds of light. According to P. VILLARD, R. W. WOOD, R LUTHER, and W. A. USCHKOFF they show no HERSCHEL's effect in the case of secondary exposure. This cannot be ascribed to total non-sensitiveness of the a silver subhaloid to Röntgen rays. It is true, F. HAUSMANN [2]) and others stated that Röntgen rays produced no solarization, and consequently that there was no formation of β silver subhaloid, but P. H. EYKMAN [3]), and subsequently K. SCHAUM and W. BRAUN [4]) could show that they do. So the silver subhaloid is also sensitive to Röntgen rays, and the non-appearance of HERSCHEL's effect must be put down to the cause that for Röntgen rays the silver haloid has a liminal value as great as, or greater than the photochemical induction of the a silver subhaloid. It is therefore assumed that in the case of röntgenography the intermittent exposure, apart from the photographic induction to be exceeded each time, does not produce a photographic effect that remains below that of a continuous irradiation.

[1]) Americ. Journ. of Science 1887 ; Vol. 33; p. 363.
[2]) Fortschritte a. d. Geb. d. R.-Str. 1901; Bd. V; S. 89.
[3]) Fortschr. a d. Geb. d. R -Str. 1902, Bd. V, Heft 4.
[4]) Zeitschr. f. wiss. Phot. 1904; Bd. 1 ; S. 382.

From H. Luggin's modified proposition it appears clearly, how the chemical sensitizers promote the photochemical decomposition process of the silver haloids by halogen absorption. They consequently prevent regression.

Lüppo-Cramer [1]) describes the following experiment, which confirms this. Precipitated silver chloride shows neither with silver nitrate, nor with ammonia, both chloride absorbents, any increased sensitiveness to light when photochemically decomposed; in an emulsion where the rapid escape of the liberated halogen is prevented, the action of the chemical sensitizer is therefore observed. From this it follows that the chemical sensitizer does not react upon the silver haloid itself at all.

Even from the considerable deviations from the reciprocity rule in a silver bromide gelatine plate with very low light intensities it follows that gelatine is not a chemical sensitizer, which has also been proved in another way, experimentally, by Lüppo-Cramer.[2])

While the chemical sensitizers act very favourably in the printing-out process, they have no, or even a detrimental influence in the case of silver haloid emulsions intended for development, as has been pointed out by Lüppo-Cramer [3]). If it is borne in mind that the α silver subhaloid germ itself is a substance very sensitive to light, which with loss of halogen, passes into the β zilver subhaloid without germinative property, it is clear that a too active chemical sensitizer does not promote reducibleness.

A number of chemical sensitizers, however, are oxidizers at the same time. From what has been said above it has appeared that oxidation transforms the β silver subhaloid into α silver subhaloid (neutralization of solarization), which may be thus represented: β silver subhaloid + oxygen = silver oxide (Ag_2O ?) + α silver subhaloid.

This reaction seems to proceed very slowly in the case of sub-bromides.

Owing to this complications may arise, so that the chemical sensitizer, while on one hand promoting the photochemical reduction, on the other hand again partly oxidizes the silver subhaloid that has been formed. Here the action of the chemical sensitizer is favourable for the process of development, as in the case of the

[1]) Phot. Korresp. 1901; S. 224.

Lüppo-Cramer. Wissensch. Arbeiten 1902; S. 87.

J. M. Eder. Jahrb. f. Phot. u. Repr. 1906; S. 648.

[2]) Lüppo-Cramer. Phot. Probleme. 1907; S. 33.

[3]) Phot. Korresp. 1903; S. 25.

silver iodide collodion plate with silver nitrate, which in the presence of light is a powerful oxidizer [1]), and the question is whether the so-called neutralization of solarization by silver nitrate is not to be ascribed to this as well, and consequently is real neutralization.

If silver haloids are allowed to be photo-chemically decomposed, the great influence of the size of the grain at once becomes evident. While fine grain silver chloride or bromide is decomposed rapidly, the latter even more rapidly than the former, the directly visible decomposition in the case of course-grain silver haloids is slower. This can at once be accounted for by H. LUGGIN's modified rule. At the surface of the silver haloid grain the liberated halogen can escape more easily, or enter into composition; inside the grain it acts regressively, so that the progression will decrease from the surface to the centre.

H. LUGGIN [2]), too, refers to the same thing in the case of silver iodide. But even if it is in a very finely divided condition, the directly visible photo-chemical decomposition does not take place rapidly. Owing to its greater atomic weight the liberated iodine not only diffuses more slowly, but moreover it is a solid substance. By absorption of this iodine, e. g. by silver nitrate, the directly visible photo-chemical decomposition at once becomes more rapid, so that it is clear why a silver haloid which is more sensitive may all the same yield a less advanced photo-chemical decomposition.

The surface decomposition of the silver haloid grain at the same time points to the fact that here, too, the "seat of the latent image is to be looked for. This is also to be inferred from further data. Thus the deposits of reduced silver haloids discovered by W. SCHERFER [3]) always start from the surface of the silver haloid grain, which appears from a microphotograph published by him. Further LÜPPO-CRAMER [4]) pointed to the dependence of the quantity of dye in the case of optical sensitization upon the surface to be coloured (i. e. upon the size of the grain) with silver chloride and silver bromide.

When it has been pointed out that in the appearance of solarization by primary fixation and secondary development the existence of a

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[1]) M. CAREY LEA (Phot, Korresp. 1887; S. 346) and LÜPPO-CRAMER (Phot. Korresp. 1907; S. 538) showed that silver subiodide is a substance which is extremely easily oxidized.

[2]) Zeitschr. f. phys. Chemie. 1897; Bd. 23; S. 611.

[3]) Phot. Rundschau. 1907; Heft 6.

[4]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 58.

    „   „   „   „   „   „   1905; S. 61.

silver subhaloid can be proved, this is not enough to account for the solarization phenomenon.

In order to illustrate this let us assume a photo-chemical decomposition with direct recomposition of the liberated halogen.

If the exposure of a photographic plate is prolonged, the silver haloid will keep forming α silver subhaloid, which is the germ for development. From HERSCHEL's effect, however, it appears that this α silver subhaloid in itself is a highly light-sensitive compound, so that it is not to be assumed that a continual accumulation of germs is taking place. Consequently the α silver subhaloid rapidly decomposes into β silver subhaloid and halogen. At the surface of the silver haloid grains a condition therefore arises in which the number of germs present depends upon formation and destruction.

If the quantity of the remaining grain surface silver subhaloid decreases, the quantitative formation of α silver subhaloid will also decrease, and as the latter itself is highly sensitive to light, the consequence of this will also be a quantitative decrease of the number of remaining germs, in other words, the reducibleness will decrease, i. e. solarization will set in.

This phenomenon is, therefore, entirely dependent upon the available surface of the grain (size of the grain). In his experimental researches LÜPPO-CRAMER [1]) repeatedly pointed to this fact.

In reality this, of course, does not take place so rapidly. The various makes of plates have chemical sensitizers which differ from each other (qualitatively and quantitatively). This, together with the prevention of diffusion, is the reason why the different commercial plates begin to get solarized after mutually different exposures.

The thiosulphate reaction shows peculiarities which can be accounted for now. The subhaloids are decomposed by the action of thiosulphate into silver and halogen silver, which after being converted into silver thiosulphate, dissolves as a double salt. The place of the α silver subhaloid germ and the β silver subhaloid is consequently taken by silver, which also possesses the property of germination, as appears from the development of primarily fixed plates. . Strong solarization, however, still produces solarization during development after primary fixation, so that the reaction between β silver subhaloid and the thiosulphate in the binding material is a slow one, as is the oxidation process already referred to. So if a highly sensitive course

[1]) Phot. Korresp. 1901; S. 350.

LÜPPO-CRAMER. Wissensch. Arbeiten. 1902; S. 41.

LÜPPO-CRAMER. Phot. Probleme 1907; S. 146.

grain plate, i. e. one with a small grain surface, in other words, with a small quantity of β silver subhaloid, which has been exposed till solarization has set in, is treated, the reaction in the gelatine will be complete sooner than with a greater quantity of β silver subhaloid in the same gelatine plate, as is the case with fine grain emulsions. The reducibleness will consequently show an increase (not to be confounded with acceleration), so that in proportion to the strength of the thiosulphate solution employed, and the duration of the action, the solarization will be removed, either to a smaller or to a greater extent, or totally.

This phenomenon was observed experimentally by KOGELMAN [1]), VIDAL [2]) and E. ENGLISCH [3]), while LÜPPO CRAMER [4]) could not demonstrate solarization at all with primarily fixed, highly sensitive, coarse-grain plates, which fix more slowly than fine-grain ones.

Sulphocyanides act analogously in reducing solarization.

In the case of SABATIER's polarization the strong decrease (disappearance ?) of development of the image after it has appeared is not to be ascribed to the decrease of the number of germs, as they have already fulfilled their function [5]). So the decrease of development can only be a reduction of the speed of development, which is to be accounted for by a strong decrease in the supply of feeding substance. From the theory given above of the so-called chemical method of development it has appeared that the silver subhaloid proves to be less soluble in the developer than the silver haloid. Therefore the more soluble silver haloid can, after reduction, be precipitated upon the germ, which still remains unchanged in its place. Consequently if the secondary exposure is of an intense nature, the feeding substance will be enveloped by subhaloid, by which development is retarded. This will take place in the developer all the more readily, because it is an absorbent of halogen.

In conclusion reference may be made to a possible explanation of the variations in the optical sensitizing of the photographic plate which is characterized by a considerable decrease in reducibleness being noticeable in the places where the power of absorption is spec-

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[1]) J. M. EDER. Jahrb. f. Phot. u Repr. 1895; S. 419.

[2]) Bull. Soc. franç. Phot. 1898; p. 583.

[3]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1901; S. 608.
             „   „ „ „ „ „   1902: S. 79.
             „   „ „ „ „ „   1904; S. 423.

[4]) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 150.

[5]) So far there is not a single reason for assuming that this reduced substance consists exclusively of α silver subhaloid germs, which pass into β silver subhaloid by the secondary exposure, by which further development would be checked.

trally highest. From M. ANDRESEN's experiments [1]) it appears that the photo-chemical decomposition products remain in contact with the dyestuff, so that the α silver subhaloid obtains a different colour sensitiveness. In this case complications may occur, if the dye is at the same time an absorbent of halogen (a chemical sensitizer), by which it changes or loses its absorption spectrum, and a consequent promotion of the photo-chemical decomposition action sets in.

VI. *Conclusions.*

From what has been said a few conclusions may be drawn, which may be of importance in practice.

Both α silver subbromide and iodide are substances of a much greater sensitiveness to light than the corresponding silver haloid.

Consequently if it was possible to compose emulsions in which these substances were present side by side with the silver haloid which as feeding substance is indispensable for development, plates would be obtained not only of a higher sensitiveness than the present ones, but in them a chemical sensitizer would be practically desirable in every respect to prevent regression. Such plates would entirely comply with the reciprocity rule, and would render the light gradations of the objects to be photographed much more correctly, which may be of great value to astronomical photography, e.g. for the determination of the light intensity of stars by the photo-chemical method (Photometry).

The α silver subhaloid can be optically sensitized, so that its application might obtain a great extension. The exact colour sensitiveness of the α silver subhaloid separately is not yet known exactly. (That in the case of secondary exposure the highest sensitiveness is situated in the red, the lowest in the green, points with great probability to the α silver subhaloid being a green substance). The experiments mentioned indicate everywhere only the difference in light sensitiveness between silver haloid and the α silver subhaloid. The greater this difference, the more favourable the result obtained. Consequently the best expectations might be entertained with respect to silver chloride plates with α silver subiodide, and it is an open question whether the latter may not be allowed to ripen too.' The β-silver subhaloid seems to possess, photo-chemically, an extremely low sensitiveness, which can only be advantageous in practice.

This process yields directly polarized copies (positives through the

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[6]) Phot. Korresp. 1898; S. 504.

camera). On one hand this seems an objection, as all printing methods are based upon the production of normal copies (the negative process). But it should be borne in mind that hitherto very few researches have been made in this domain.

For direct colour photography [1]) with colour elements lying side by side under the emulsion, according to L. Ducos du Hauron's system (which especially lately has given promise of a great future), which requires directly polarized copies, and which so far has only succeeded in obtaining them in an indirect way, this method would also be practically valuable.

In this direction little experimenting has hitherto been done from a photo-chemical point of view, and even in what has been done it has been impossible to account for the phenomena that occurred, so that for the present there is no need for us to take too pessimistic a standpoint with reference to this.

VII. *The shape of the image in the case of Herschel's effect.*

As to the shape of the image in the case of Herschel's effect fig. 8 may be referred to.

It is clear that after the critical exposure the normal copy is again a surface image. If a considerable portion of the surface silver haloid present has already been decomposed into a silver subhaloid and halogen, the secondary exposure will not be able again to form as much a silver subhaloid as would have been the case if the primary exposure had not taken place. A negative is obtained then the density of which is less than that of a plate not previously exposed. This case presents itself in the sky a in fig. 5.

Advanced primary exposure may result in solarization, in which case the surface silver haloid can no longer supply the same quantity of germs as was present before: Herschel's effect then coalesces with solarisation, and the critical exposure can no longer be ascertained.

The greater light sensitiveness of the a silver subhaloid as compared

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[1]) I expressly call this method "direct", because I cannot agree to the judgment of a number of others, who want to classify it among the indirect methods. They say that it is not direct colour photography, but three-colour photography, ignoring the fact that the bleaching method which is reckoned to belong to the direct methods, is also three-colour photography. Nor can I agree to A. v. Hübl's classification (Phot. Rundschau, 1908, p. 2), by which the bleaching process would be assigned to the indirect methods. The fact of the matter is that the difference is only a question of method, i.e. whether the colours are obtained directly after exposure (with development), or only through subsequent addition.
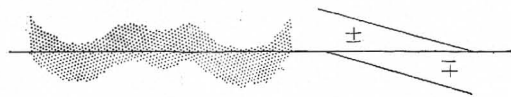
A. P. H. TRIVELLI. "A contribution to our knowledge of the solarization phenomenon and of some other properties of the latent image."
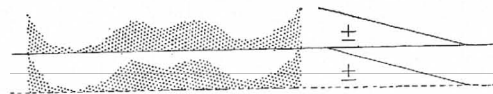

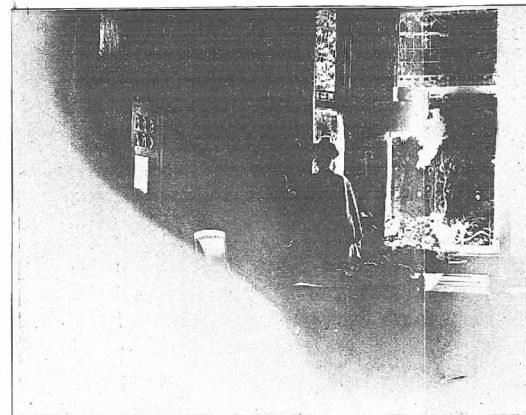Fig. 1.

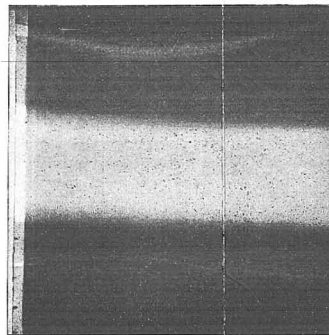Fig. 2.

Fig. 3.

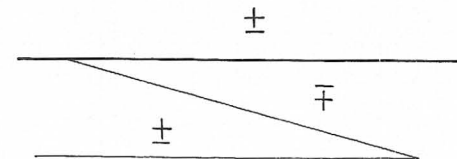Fig. 4.

Fig. 5.

Fig. 6

Fig. 7.

Fig. 8.

with that of silver haloid is also shown in the amount of halation. In fig. 5 the foliage of the tree is affected by it, while the houses round the sky near a do not show any; there the halation was too slight to exceed the liminal value of the silver haloid. In fig. 6 the dark 'lead frame of the window also shows the destruction of the germ owing to halation; on the other hand on the right side it was able to form fresh germs through a more powerful action.

That the difference in light sensitiveness between the germ and the silver haloid is great, appears from the backs of the dogs, and from the shoulders of the female figure to the right in fig. 5. The narrow white strip indicates that after the germs had been totally destroyed at the free surface, for some time longer the silver haloid again began to supply germs, first in the most strongly exposed portions, and then gradually also in those which received less exposure. Consequently if the action of the light increases, these strips must become narrower, which is also shown by the figure, as the dog to the left was more glossy than the one to the right.

The white strips along the edges of the black objects in the background are of quite a different nature. These are to be ascribed entirely to irradiation, for in the case of stronger light intensities occurring side by side they are broader than where the intensity is less great.

If observed very closely by light reflected at an angle, these bright strips are seen to possess a greater gloss than the portions immediately adjoining them. To the left of the tree top this is easier to see than to the right. The light from the wall has acted more intensely to the left than to the right, and notwithstanding the polarization a copy of greater density is shown there. That the critical exposure should have been surpassed, is out of the question here.

This phenomenon, too, can be accounted for according to the theory given, for in this theory it has been stated, that the critical exposure is not surpassed till the secondary exposure has formed a greater amount of a silver subhaloid than is present in consequence of the primary exposure. Consequently after the liminal value of the silver haloid has been surpassed, a new surface image can originate, the density can increase afresh, and still at the same time the copy will remain polarized.

All the abnormalities in the figures 5 and 6 have thus been accounted for.

In conclusion I wish to express my best thanks to Mr. P. H. EYKMAN for finding materials and placing them at my disposal, and for his constant interest in my work.