Reversible Photolysis of Ag Sorbed on Collodial Metal Oxides

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The photolysis of Ag sorbed on small particles of ZnO and TiO_2 in two allotropic modifications is described, also the preparation of photosensitive surface complexes of this type. Gels of such materials are found to change their diffuse reflecting power for light (relative albedo) permanently upon exposure to radiation of wave-lengths up to approximately 5800A. It is possible to obtain with these materials photographic surface images without microscopically resolvable structure. The dependence of the maximal relative albedo variation (80 percent) upon the Ag concentration is found to be that corresponding to a monolayer of Ag atoms. The albedo change is interpreted as a culminative photolysis of the monolayer on the particles exposed to the radiation. This photolysis is reversible upon contact with traces of H_2O_2 or O_3. The reversion reestablishes the original photo-sensitive qualities so that the whole process can be repeated many times. A hypothesis of the mechanism of this effect is presented.

A. INTRODUCTION

THE observation that a finely divided suspension of crystalline zinc oxide (ZnO) in water was rapidly darkened when exposed to white light if a small quantity of a silver salt ($AgNO_3$) was in solution was first described by G. Tammann.[1]

Kohlschuetter and d'Almendra[2] repeated the experiments of Tammann under more carefully controlled conditions and proved that the blackening of the suspended particles was caused by crystals of metallic silver which formed at the surface of the ZnO crystals in an extremely finely divided form. If the silver salt in solution was present in a sufficient concentration, the growth of fine fibrous Ag crystals starting from the ZnO base could be observed with a microscope under the influence of the illuminating light.

Perret[3] could show that silver ions in a saturated solution of silver oxide (Ag_2O), i.e., in a concentration of 1.3×10^{-5}, was sufficient to induce this photosensitivity.

The authors have found that this effect is not characteristic only for ZnO, but also to numerous other insoluble (white), amphoteric metal oxides as well, such as TiO_2, SiO_2, $Al(OH)_3$, Al_2O_3, etc.

In view of the lack of any photosensitivity of the suspended metal oxides in the absence of silver, as well as of the silver ion of the dissociated silver salt in solution, the almost spontaneously induced sensitivity to light of the metal oxide particles in the presence of silver suggests a photo-reaction upon the surface of the individual oxide crystals, quite different from the usual photolysis of Ag compounds such as the halides, etc. This difference is further emphasized by the existence of a complete reversibility of this type of reaction, not known for the normal photolytic decomposition of silver compounds.

It has been the purpose of the investigation described here to gain an insight particularly into the physical nature of these photosensitive surface layers.

B. EXPERIMENTAL PROCEDURE

1. Materials and Method of Preparation

The preparation of the photosensitive material involves, obviously, a reaction by which Ag—as ion or as molecule—becomes attached to the particle surfaces of a finely divided substrate, which consists of a metal oxide. The substrate particle acts, therefore, as a carrier substance and great care has to be taken that this substance is chemically as pure as possible. Of the large variety of carrier substances possible, only zinc

[1] G. Tammann, Zeits. f. anorg. Chemie **114**, 151 (1920).
[2] V. Kohlschuetter and d'Almendra, Ber. d. D. Chem. Ges. **54**, 1961 (1921).
[3] A. Perret, J. Chim. Phys. **23**, 97 (1926).

oxide and titanium dioxide were used in the experiments described here for the reason that the former can be obtained in sufficient purity and at the same time in a large variation of particle sizes and shapes, whereas the latter (TiO_2), though less pure, was available in the same particle size distribution in two allotropic modifications, i.e., as anatase and as rutile. The latter variation was of special interest since it permitted the study of two different crystal lattices of the same substance.

As a ZnO substrate, a material with an average particle size diameter of 0.3μ was used; the particle size distribution of this material was not known (CP Baker's Laboratory Chemical Reagents).

As TiO_2, a material was used which contained a trace of Pb and As (<20 p.p.m.). The particle size distribution is given in Fig. 1 for both modifications as derived from fractionated centrifugation and by direct microscopic count. It indicates that the maximum for both materials lies at about 0.3μ, and that the anatase has a larger fraction of small particles than the rutile.

The silver was introduced as oxide (Ag_2O, CP) in order to avoid, after the completion of the sorption process, the presence of any anion other than OH^- as by-product of the surface reaction.[4]

Since Ag_2O has a very limited solubility, a concentrated gel-like suspension of the substrate in distilled water was agitated violently with high speed homogenizers, followed sometimes by passage through a colloid mill, in the presence of a known quantity of finely divided Ag_2O. The agitation of the slurry was continued until microscopic investigation indicated the disappearance of the major part of the silver oxide crystals.[5] The slurry was then exposed for several hours to elevated temperature (45°–55°C) to allow for adequate diffusion of the available Ag and for the attainment of an equilibrium. The slurry was then poured in a flat dish and dried at 50°–60°C in an air stream. The dried cake was ground in a mortar (agate) to a fine powder and stored in dark glass containers.

The resulting reaction between the substrate and silver goes obviously as follows: The silver oxide particle dissolves gradually in the free water of the slurry. Since the solubility of Ag_2O is quite low (13 mg per liter), the rate of dissolution (as AgOH) will be quite slow. Since the particle is surrounded by metal oxides, the Ag

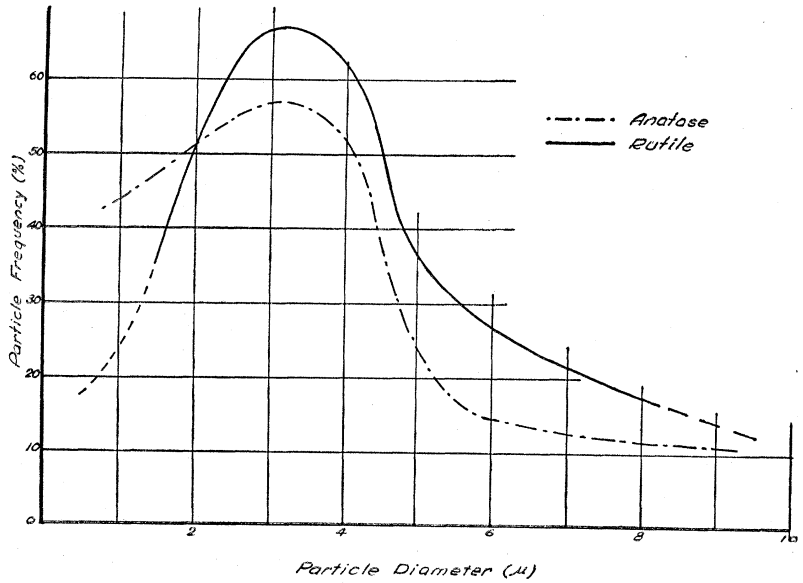


FIG. 1. Particle size distribution for TiO_2 as anatase and rutile. The curves are derived from the average values obtained by fractionated centrifugation and by direct microscopic count.

[4] Most previous workers used $AgNO_3$ which, upon sorption of the Ag on the substrate surface, possibly by an ion-exchange process, resulted in the formation of either HNO_3 or a nitrate which remained in suspension. The use of Ag_2O can only result in H_2O, and if necessary, a residue of undissociated Ag_2O.

[5] Great care had to be taken to avoid the presence of other metal ions; therefore, the high speed homogenizer had to be specially constructed of stainless steel.

will be sorbed in a manner not known in detail. If by adequate agitation of the slurry, the surface of all the individual particles has gradually been made available to the dissolved AgOH, a uniformity of the Ag concentration on the surface of each particle is obtained. The necessity of observing this particular condition carefully is obvious since the total surface area of the substrate particles of these materials is of the order of 5×10^4 cm^2/g.

It is noteworthy that the surface reaction between both almost insoluble (in the case of TiO_2, entirely insoluble) components must proceed very rapidly since these preparations become photosensitive within the first few minutes of homogenization. Preparations for quantitative measurements have, therefore, to be made in the dark.

2. Apparatus for Measurement of Photo-Sensitivity

Because of the high index of refraction[6] and the resulting large light scattering quality, even thin layers of the materials as dry powders and as gels are intransparent and appear uniformly white or grayish-white. Any measurement of the photo-sensitivity has to be thus based on the determination of the reflectivity for scattered light resulting in a measurement of the albedo on a relative scale.

In order to facilitate this, an optical system was designed, shown schematically in Fig. 2, where the source "*S*" consisted of a 200-watt d.c. tungsten arc lamp, a large condenser "*C*," a cuvette "*G*" containing a dilute aqueous $CuSO_4$ solution, an achromatic objective "O_1" which formed an image of the anode disk of the arc on the horizontal specimen holder "*H*." Between "O_1" and "*H*" was interposed a mirror "*M*" in order to permit the horizontal position of the sample (necessary on account of the semi-liquid nature of the sample). The sample reflected the light diffusely; a section of it, leaving at an angle of approximately 45°, passed through objective "O_2" and was collected on a sensitive photo-voltaic cell (Lange) "*P*." This cell was connected with a sensitive millivolt meter "*V*" (sensitivity $\pm$0.1 mv) which measured thus the intensity of the diffusely reflected light (albedo) at 45°. The whole apparatus was protected against stray radiation.

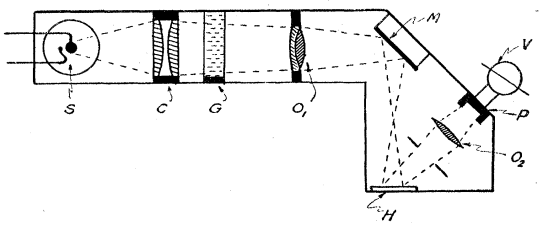


FIG. 2. Optical arrangement for the measurement of albedo variation: (*S*) tungsten arc lamp; (*C*) condensers; (*G*) $CuSO_4$ filter cell; (O_1) achromatic objective; (*M*) mirror; (*H*) sample of plaster of Paris standard; (O_2) collecting lens; (*P*) photo-voltaic cell; (*V*) millivoltmeter.

As an albedo standard, a cast plaster of Paris plate was put in the position of "*H*" to standardize the intensity of the light source. The stability of the latter was accomplished by ballasting resistances. Readings on the standard were always taken before and after a run in order to check for a variation of "*S*" during the intervals. If (both) readings agreed, it was assumed that the light sensitivity had remained constant during the measurement.

The sensitivity curve of the photo-voltaic cell is a linear function of the light intensity in the region used in these experiments; therefore these measurements result in the direct determination of the decrease of the relative albedo as function of time of exposure for the spectral nature of the radiation of the arc lamp.

In order to determine qualitatively the dependence of the albedo variation with the wavelength of the illuminating light, a prism spectrograph was assembled which projected the spectrum of a d.c. carbon arc or a 400-watt a.c. mercury arc upon a slide carrying a thin layer of the photosensitive material. The spectrograph was arranged in the usual manner, the light passing through a condensing lens, a liquid filter, slit, collimating lens, 60° flint prism 6 cm square, objective. The exposure required 10–20 minutes.

In order to determine the maximal albedo variation, i.e., to obtain the maximum darkening of a sample, a mercury arc was used, mounted in a camera so that the arc light reflected by a mirror could strike the sample without its being

[6] The indices of refraction are: for ZnO = 2.0, for TiO_2 anatase = 2.5, and for TiO_2 rutile = 2.8.

exposed to the stray light. Maximum darkening was obtained here in general after 5–7 minutes exposure.

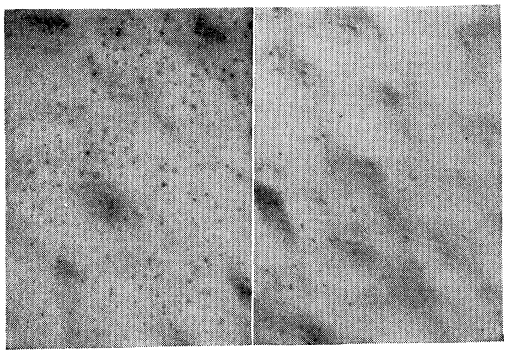
C. RESULTS

1. General Description

The photosensitivity of the preparations is very low or probably even absent in complete absence of moisture; hence, the materials were always tested in the form of an aqueous gel so viscous that it could be applied as a uniform layer on a glass plate (microslide). Since these layers were opaque, all microscopic examinations had to be performed with reflected light.[7]

If a freshly prepared, undigested, silver surface compound with either ZnO or TiO_2 as substrate is examined microscopically, there can be observed in the white field numerous minute specks of dark particles of unreacted silver oxide. The frequency of these particles depends upon the initial concentration of Ag_2O in the sample. Figures 3a and 4a illustrate this state.[8]

The same material, when completely homogenized and digested, shows only traces of free Ag_2O particles (Fig. 3b) or none at all (Fig. 4b), provided that the Ag concentration in the preparation remains sufficiently small.



(a) (b)

FIG. 3. Photo-sensitive gel on ZnO substrate (2 percent Ag_2O) 84×, Zeiss Ultrapak dark-field illumination. (a) Immediately after homogenization. (b) After 37-hour digestion. Note the presence of free Ag_2O particles in (a) and the almost complete disappearance in (b).

[7] Vertical illuminator or apo condenser (Zeiss), preferably with dark-field illumination.

[8] Since the use of a homogenous (water) immersion system proved unfeasible, the preparations had to be observed without cover glass, hence the surfaces of the gels were not plane and gave a wave-like impression with dark field illumination.

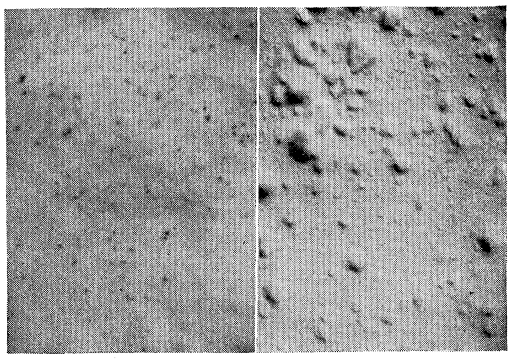
The observation of the decrease of frequency of those particles affords thus a quantitative visual evidence of the progress of the sorption process on the substrate during the various stages of preparation.[9]

Microscopic studies revealed two other significant properties:

First, even heavily exposed surfaces are blackened only within an extremely thin surface layer, probably of a thickness of only a few particle diameters. This is not surprising because of the high scattering power of the substrates which by diffuse reflection should prevent radiation energy from reaching into any depth.

Second, fully exposed surfaces show no more structural detail than the gels from an Ag-free or unexposed preparation (aside from isolated Ag_2O particles). The inspection was carried to optical resolving powers with a 3-mm apochromatic immersion objective (num. apert. $=1.4$) which should at least indicate details of a magnitude of 0.3μ. If the cause of the blackening of the surface is "reduced" Ag, the particles resulting must thus be much smaller than the average particle size of the substrate.

The lack of optically resolvable detail in these blackened photosensitive surfaces suggests the possibility of utilizing such gels for microphoto-



(a) (b)

FIG. 4. Photo-sensitive gel on TiO_2 (anatase) substrate (2 percent Ag_2O) 84×, Zeiss Ultrapak dark-field illumination. (a) Immediately after homogenization. (b) After 37-hour digestion. Note the presence of free Ag_2O particles in (a) and the complete absence in (b).

[9] This gradual disappearance of free Ag_2O is paralleled by a decrease of hydroxyl ion concentration within the gel. A detailed description of these phenomena ("Sludge pH" variations) will be published elsewhere.

graphic purposes. In order to test the order of magnitude of the photographic resolving power, samples of an Ag-rutile gel (chosen because of its maximal contrast between white and black) were placed in the focal plane of a camera objective particularly excelling in linear definition ("Collinear" 1:5.8, Voigtlander). A photographic replica of a cross-grating of equal width of white and black lines (70 lines per cm, 45-cm diameter), illuminated by a point light source and condenser, was the optical object. The resulting image on the gel, which was reduced about 12× linear, was inspected under the microscope (yellow filter, apo condenser).

Aside from occasional imperfection of the surface due to the unevenness of the gel, the images were perfect and strong in contrast. Particular attention was put on the shape of the intersections of the lines of the cross-grating, which did not show any observable distortion. No limit of resolution down to the lower limit of the optical resolving power of the microscope objective used (num. apert. = 0.94) could be found. Considering the particular conditions of dark-field illumination, this would correspond approximately to the wave-length of the light used for microscopic illumination, i.e., 0.5μ. In the usual terms this would indicate that a limit of the resolving power was not yet found at a detail corresponding to 800–1000 lines per mm. This photographic resolving power appears thus to be of the order of magnitude described by Goldberg[10] and Narath[11] for certain photographic emulsions of the Lippmann type.

The final color to which these photosensitive materials darken varies greatly with the Ag concentration and the nature of the substrate from a complete black to brownish-gray, and even to a yellowish color. This is particularly evident if ZnO preparations are used of different particle sizes. A ZnO preparation of the finest particle size available (anisometric particles 0.15μ long and 0.05μ wide)[12] showed upon prolonged exposure a deep yellow, whereas for the same Ag concentration and the same exposure, a ZnO preparation (of equal chemical purity) produced a blackish-brown color.

The particle size of the substrate appears thus to be a determining factor in the color of the exposed surface, and the variation of color with increasing particle sizes seems to follow approximately the color sequence observed in gelatin suspensions of submicroscopic colloidal silver particles exposed to conditions under which the individual Ag particle increases in size.[13] The color for the finest particles is yellow; that for the largest is blue-black.

All samples, regardless of the stage of the process of preparation, were photosensitive. At the early stages of processing they darken to a lesser extent, when exposed to light, than the thoroughly digested samples where the completion of the surface reaction is indicated by the absence of Ag_2O particles. It appears, thus, that immediately upon contact between the substrate particles and Ag_2O in the presence of moisture, there occurs a surface reaction upon which the silver is sorbed. This reaction is aided by an intense agitation of the components. The rapidity of this initial sorption decreases substantially in the later stages of the process until a "saturation" of Ag on the particle surfaces occurs, provided that the initial Ag_2O concentration was sufficient. If an excess of Ag_2O was added, a complete disappearance of the particles can no longer be observed.

In all experiments, the concentration of Ag_2O (black) did not exceed 10 percent of the mass of the (white) substrate. Since the specific gravities are, for Ag_2O 7.1, for ZnO 5.4, for TiO_2 3.8 (anatase) and 4.3 (rutile), the volume of the black component was at the most 6 percent of the white, i.e., at the highest Ag concentration used, 94 percent of the particles were white and 6 percent were dark (assuming equal particle sizes). Consequently, the whiteness of the initial mixture was barely less than that of the substrate without silver. Since pure Ag_2O is not photosensitive either in the dry or in the moist state[2,14] an unreacted mixture of both components should not show any appreciable change of albedo. This can be demonstrated on initial mixtures of carefully dried components, but

[10] E. Goldberg, Zeits. f. tech. Physik **7**, 500 (1926).
[11] A. Narath, II Congr. Int. Phot. Paris, p. 297 (1936). A. Narath, Kinotech **17**, 51 (1935).
[12] Courtesy of the Research Division of the New Jersey Zinc Company, Palmerton, Pennsylvania.
[13] R. Zsigmondy, Kolloidchemie, 190 (1920).
[14] R. Berthelot, Comptes rendus **127**, 156 (1898).

even these mixtures darken upon prolonged exposure to light, apparently under the influence of the moisture of the air which apparently supplies enough H_2O for the initial stages of the sorption reaction.

2. Variation of Albedo

In order to study the dependence of the photosensitivity on the presence of moisture, a set of three samples of TiO_2, as anatase and rutile, and of ZnO, containing 5 percent Ag_2O, respectively, were treated as follows: After preparing the specimens and spreading them on glass plates, they were first air-dried for one day, and subsequently desiccated over $CaCl_2$ for about 7–8 days; all manipulation was performed in the absence of light. The albedo of each sample was determined prior to the exposure to light (A_0). Each sample was then exposed to the light from the carbon arc source for 5 minutes; this exposure was interrupted each minute and the albedo determined.

All samples showed an albedo decrease after the first exposure. The final values in terms of A_1/A_0 (A_1 final, A_0 initial albedo) were:

ZnO	73.8 percent,
TiO_2 (anatase)	84.2 percent,
TiO_2 (rutile)	40.3 percent.

The above experiment indicates that even at the very low moisture content obtained by drying over $CaCl_2$ the compounds were slightly photosensitive. No experiments with high vacuum desiccation and exposure under controlled dry conditions were attempted because of certain other surface effects (see below).

It is significant that, by adding a small amount of H_2O to the dried sample (by placing a small drop on the surface), it becomes extremely sensitive and darkens instantaneously. In all cases the photosentivity proved many times larger when the preparation was used as an aqueous gel.

Not less striking is the dependence of A_1/A_0 upon the Ag concentration of materials in gel form. This relationship was determined by the above method for a series of 20 samples of ZnO and TiO_2 (anatase and rutile) with varying silver concentrations.

For this purpose it proved to be advantageous to expose the samples first to a strong light source in order to obtain in a minimum of time the maximum decrease of albedo. This was accomplished by exposing the sample for 10 minutes to a mercury arc in the previously described manner. The relative albedos before (A_0) and after (A_1) this exposure were measured on samples ranging from 0.5 percent to 10 percent Ag concentration. The results are shown in Fig. 5 and indicate that, if at all, A_1/A_0 varies only little with an Ag concentration above 1 percent, but that below this value the variatioll is very large indeed. As a matter of fact, an "blackening" of which a particular substrate is capable appears to occur with about 1 percent Ag concentration, according to the indication of the instrument. Subjective observation reveals a noticeable color variation between exposed samples of the same substrate with different Ag concentrations above 1 percent. Figure 5 shows the largest A_1/A_0 for rutile (also a small decrease beyond 1 percent from 0.2 to 0.07, which appears larger than the over-all margin of experimental error in this region). This is in agreement with the previous result obtained from dried samples (0.4).

Anatase shows no variation if the linear interpolation for the A_1/A_0 values between 1 percent and 3.5 percent is approximately correct.

For ZnO practically all blackening has occurred at 0.5 percent Ag. At higher concentrations the values are much more scattered—a fact which is quite characteristic for ZnO substrates (see below).

These findings lead to the following consideration: The known particle size distribution (Fig. 1) of the substrates results in an average particle size for all three types as 3×10^{-5} cm, neglecting possibly different shapes. The total surface (S_t) of 1 gram of dry substrate of an average particle diameter (d_p) and a specific gravity (δ), assuming spherical shapes, is $S_t=6/(\delta\cdot d_p)$. One g Ag_2O contains 0.93 g Ag which covers an area of $S_{Ag}=0.93\cdot N_A\cdot d_{Ag}{}^2/108$, where N_A is Avogadro's number and d_{Ag} the atomic (or ionic) diameter.

The quantity Q (in grams) of Ag_2O required to cover S_t is thus:

$$Q=\frac{6\cdot108}{0.93\cdot N_A\cdot\delta\cdot d_p\cdot d_{Ag}{}^2}=\frac{3.83\cdot10^{-15}}{\delta\cdot d_{Ag}{}^2}.$$

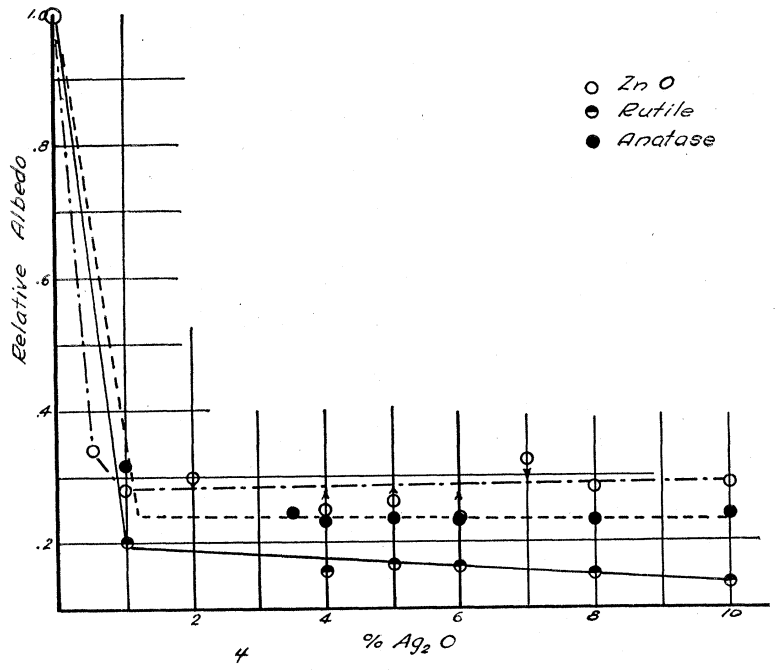


FIG. 5. Relative albedo (A_1/A_0) *vs.* Ag concentration on three different substrates. The interpolation between the points is assumed to be linear in first approximation.

If the values of 1.44A and 1.26A are taken for the respective radii of Ag and Ag^+, 1 g Ag covers 4.27×10^6 cm² as monatomic and 3.35×10^6 cm² as monionic layer. Table I gives the calculated data:

TABLE I.

Substrate	$d_p(\mu)$	δ	S_i(cm²)	Q_{Ag}(%)	Q_{Ag^+}(%)
ZnO	0.3	2.56	78,000	1.82	2.47
TiO_2 (anatase)	0.3	3.84	52,000	1.2	1.65
TiO_2 (rutile)	0.3	4.26	47,000	1.09	1.49

Comparison of the Q values with the Ag concentrations (Fig. 5) at which the variation of A_1/A_0 decreases rapidly indicates that for ZnO this point is reached between 0.5 and 1 percent, for anatase (interpolated) between 1 and 1.5 percent, and for rutile at 1 percent or below.[15]

Both TiO_2 modifications indicate thus a very sharp change at an Ag concentration which corresponds to a monatomic layer. This is not true for ZnO where this concentration falls into the range of one half of the calculated value for complete surface occupation. This may be because of the unknown particle size distribution of the ZnO substrate used or, more likely, because of the fact that Zn is 2-valent while Ti is 4-valent; thus ZnO may only be capable of sorbing at the same particle surface area one-half of the Ag atoms which TiO_2 can hold.

[15] Unfortunately, there were no samples of TiO_2 available with an Ag_2O concentration of less than 1 percent; subsequent data, however, confirm the assumption that for rutile, for example, the sharp change of the curve lies at approximately 1 percent Ag_2O.

3. Spectral Sensitivity

The spectral sensitivity was determined by exposing the gels on glass slides to a spectrum obtained from the prism spectrograph described above with an Hg arc as source. A clear (negative) image of the visible part of the Hg line spectrum resulted; this was superimposed on a continuum. Figure 6a-d shows an enlarged (2×) set of negatives of photographs of such spectral images on ZnO, anatase and rutile, in comparison with a normal photographic reproduction.

It was apparent that there existed no definite limit of the sensitivity up to 5800A; consequently, the main Hg lines could be traced throughout the spectral image up to 5791A, indicating a continuous photosensitivity at least into the yellow-green region. Furthermore, a distinct band was present in the spectral image on all three different substrates, which is ab-

sent in the photographic spectrum. On the ZnO sample, this band reached from 3800A down to the absorption limit of glass; on the anatase sample, the band appeared in approximately the same region, while on the rutile substrate the band was decidedly broader and began already at 4100A, extending also to the absorption limit of glass.

Although these results can only be considered of a quantitative nature, they seem definitely to indicate the absence of a sharp decline of sensitivity in this part of the spectrum as is characteristic for the photo-chemical decomposition of Ag halides:[16] for AgCl 4000A, AgBr 4500A, AgI, 4900A. The nature of this band may be related to the work of Goodeve and Kitchener,[17] who report the long-wave absorption limit for ZnO at 3850A, and for TiO_2 as rutile at 4100A to coincide with a range wherein the surfaces of the oxide particles act as photo sensitizers.[18]

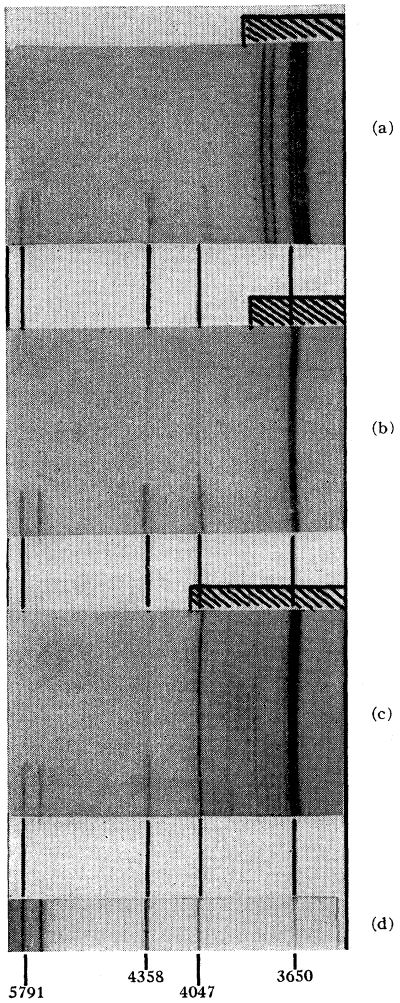


FIG. 6. Photographic reproduction of Hg-arc spectrum images (all unretouched, 2.1×magnified) on: (a) ZnO containing 1 percent Ag_2O. (b) TiO_2 as anatase containing 1 percent Ag_2O. (c) TiO_2 as rutile containing 1 percent Ag_2O. (d) Panchromatic film for comparison. The absorption bands are marked for each substrate. Since the long-wave lines are very difficult to distinguish on the photographic reproduction, they are marked in the lower half, of each photo.

Since these photo sensitive phenomena suggest obviously a reduction process of the sorbed Ag, a series of experiments were performed where the exposure of the gel specimens to the spectrum was carried out in a closed glass container filled with a controlled moist atmosphere (O_2, H_2, and He). The results showed for the same exposure time a definitely darker image in He and H_2 than in O_2, indicating that the photo-sensitivity on all substrates is dependent on the partial pressure of oxygen, an observation which supports the assumption of a reduction process.

There are also qualitative indications that the longer wave-length sensitivity was more affected by O_2 than the blue part of the spectrum.

4. The Reversion Effect

It had already been observed at an early stage of these experiments that exposed sample slides which had been dried "faded" appreciably in a few days and, after prolonged storage, lost every trace of the previous exposure. If, however, one part of the sample had been very heavily exposed, e.g., by a predominant spectral line, this line would persist. Such faded samples were just as sensitive to a subsequent, i.e., second, exposure as they had been originally. This observation indicated that the surface reaction which produces a darkening under the influence of radiation was completely reversible. The

[16] C. E. K. Mees, *Theory of the Photographic Process* (The Macmillan Company, New York, 1942), p. 962.

[17] C. F. Goodeve, Trans. Farad. Soc. **33**, 340 (1937). C. F. Goodeve and J. A. Kitchener, Trans. Farad. Soc. **34**, 902 (1938).

[18] According to this, the band would mark the region within which the substrate would, by absorption of radiation energy, cause chemical changes in its immediate environment without its undergoing an irreversible change at the end of the reaction. This process can but does not necessarily have to be a fluorescence phenomenon. It may be mentioned that the ZnO material used shows almost no fluorescence, nor does TiO_2 to any appreciable extent.

influences capable of causing this reversion were investigated in an extended series of experiments too lengthy to be described here in detail.

The significant result was that an O_2 atmosphere caused the reversion only in the presence of light, and that it was necessary to add a small quantity of O_3 to the gas atmosphere to which the specimen was exposed to produce the reversion in the dark. This indicates that the reversion consists of an oxidation process which transforms the reduced (dark) state, "*R*-state," of the Ag surface complex into an oxidized (white) state, "*O*-state," and that this oxidation process requires the presence of active oxygen.

It was also possible to produce this reversion by means of a liquid contact in the form of a solution of H_2O_2. The application of a liquid required a fixation of the substrate particles in the gel in order to assure that the identical particle surfaces were subjected to the process when the latter was repeated. After experimenting with numerous ineffective binder materials, a solution of ethylcellulose in toluene was used.[19] The prepared (air dry) sample—rutile with 10 percent Ag_2O—was suspended in the solution painted on a glass slide, and the solvent evaporated. A minute image of a cross-grating was photographed (see above) onto the exposed surface of the preparation, and subsequently a trace of a 30 percent peroxide solution was placed on the surface in such a manner that only a fraction of the image was wetted. The wetted area bleached out immediately, while the peroxide was violently decomposed into H_2O and O_2.[20]

The sample was then again exposed to the former image and a sharp and undistorted pattern resulted. This procedure could be repeated a number of times without any noticeable indication of an incomplete reversibility of the process.[21]

Since the use of ozone requires no physical disturbance of the sample surface and consequently no binding agent, the following reversion experiments were performed with the use of O_3 only:

Four samples, each containing 2 percent Ag_2O, were prepared: two on ZnO (I and II), one on anatase (III), and one on rutile (IV). All samples were exposed as a gel for 30 minutes to the Hg spectrum and were subsequently air-dried. (I) was henceforth stored in a dark, air-tight container. (II), (III), and (IV) were exposed for 10 minutes in the dark to a slow flow of oxygen, having passed through an ozonizer (7.5 kv)[22] adjusted to an approximate yield of 1.24 g O_3/hr. Immediately after this exposure very little, if any, reversion could be observed.

Samples (II), (III), and (IV) were stored, like (I), in a light-tight container and inspected at intervals by subjective comparison with (I). After 24 hours storage (II) had reversed markedly, but showed a general fog, (III) spectrum had completely disappeared—slight fog, (IV) spectrum bleached except for 4100A and 3650A lines—slight fog. After 48 hours storage (II) spectrum bleached except for major lines; (III) completely white—very white line where former 3650A line; (IV) white, except for faint black trace of 3650A line.

After 96 hours storage (II) white; very white line where former 3650A line; (III) and (IV) were again exposed to the spectrum and were found as photo-sensitive as before. (I) remained unchanged throughout.

Finally the dependence of the reversion effect with the length of the initial exposure was studied by exposing a set of 2 percent Ag_2O-ZnO samples to the spectrum at exposure times varying from 2–128 minutes. While the optimal uniform darkness was reached under these conditions with an exposure of 20–30 minutes, a prolongation produced a visible inhomogeneity of the dark regions and caused in extreme cases shiny metallic particles of microscopic size which formed the centers of dark spots and gave the exposed area a somewhat mottled appearance.

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[19] Ethylcellulose, though insoluble in water, has a high capacity for absorbed moisture.

[20] Most of these photosensitive surface complexes are very efficient decomposition promoters for peroxides in general. These properties, which show certain parallels to the photosensitivity, will be described in a separate publication.

[21] This bleaching reaction with H_2O_2 is noteworthy since H_2O_2 acts upon free silver oxide as a reducing agent, converting the latter into (dark) colloidal silver. The fact that this agent acts upon Ag in the sorbed state in the opposite sense, i.e., as an oxidizing agent, characterizes the peculiar chemical stability of the complex on the particle surface.

[22] Courtesy of the Kerkhoff Laboratories of Biology, California Institute of Technology.

These samples underwent the above ozonization process for 10 minutes. In 6 days all short exposures were reversed while the heavy exposures did not show any major change except for a partial bleaching of the mottled areas.

One can thus summarize the results as follows:

(1) The reversion consists of an oxidation process at the surface of the particle requiring active oxygen (as ozone or hydrogen peroxide).

(2) The rate of the oxidation process is dependent upon the partial pressure of O at the surface (and probably also on the presence of moisture); it is, therefore, slow for gaseous contact with O_3 and fast upon liquid contact with H_2O_2.

(3) The reversion restores to the surface the original photosensitivity. The process can thus be repeated probably indefinitely.

(4) The reversion is incomplete when the surface has previously been overexposed.

(5) The rate of reversion depends upon the nature of the substrate. The lowest rate was observed for ZnO, the fastest for anatase, rutile being slightly slower than anatase. For the 2 percent Ag_2O concentration in all tested samples this order is parallel to the respective excess of Ag_2O over the saturation values for a monolayer as indicated in Fig. 5.

D. DISCUSSION

A discussion of the phenomena described has to be based, obviously, on a more specific hypothesis concerning the nature of the surface reaction which the silver oxide undergoes with the particle surface during the process of preparation.

All three substrates are practically insoluble (TiO_2 in both modifications, entirely; ZnO with 4.5 mg per liter), while Ag_2O is soluble with 13 mg per liter. The surfaces of the substrate are probably completely hydrated upon prolonged contact with water; hence, the molecular structure of the exposed layers will resemble $Zn(OH)_2$ and $Ti(OH)_4$, respectively. Since Ag_2O (or AgOH) is a strong base, and since both substrates are of amphoteric character, i.e., can act as weak acids, the silver may become chemisorbed within the hydration layer of the particle. It is not intended to suggest the formation of an actual chemical surface compound such as an Ag-zincate or an Ag-titanate, but rather the establishment of a stability of the sorbed monolayer of Ag by chemical forces, which stability is larger than that caused by the van der Waals forces alone.[23] This layer structure would then characterize the "*O*-state."

In favor of this hypothesis is the sharp restriction of the photosensitivity to a definite Ag concentration sufficient for a complete surface layer calculated from particle sizes, and also, the fact that the bi-valent ZnO requires in fair approximation one-half of the Ag atoms of the 4-valent TiO_2 modifications in order to fill the same particle surface area.

The observation that the formation of these surface complexes is absent when other liquids free of water and/or of OH groups (pentane, benzene, toluene, etc.) are used supports the necessity for a hydrated state of the surface.

The quality of the surface complexes, most difficult to interpret on a quantitative basis, is the order of magnitude of the change which the optical surface properties undergo upon exposure to radiation.[24] This difficulty is illustrated by the following calculation:

As has been discussed above, it is likely that only the uppermost surface particles contribute to the albedo, especially in the case of rutile, which is the most sensitive substrate material. If it is furthermore assumed that in the *O*-state the surface of each particle is chemically "saturated" by a complete monolayer of Ag atoms (or AgOH molecules), this equilibrium configuration is disturbed by the excitation resulting from quantum absorption which frees the Ag atoms temporarily to migrate over the surface (but probably not beyond the particle boundaries) in order to form a more stable configuration, i.e., to coalesce into one or several minute Ag crystals (nuclei). For a particle diameter of 3×10^{-5} cm, the surface area exposed to light will be about 3×10^{-9} cm^2. As one Ag atom covers 8.3×10^{-16} cm^2, a monolayer upon the exposed particle surface will contain 3×10^{6} atoms. If these atoms

[23] On the other hand, it would not contradict the experimental findings that in the *O*-state AgOH is initially sorbed as a molecule rather than as an ion, and that upon excitation the silver ion is freed to react chemically with the substrate surface. In this case the transition from the *O* into the *R*-state would then result in the production of a water molecule for each Ag atom.

[24] The principal difference between this reaction and the well-known photolysis of Ag-halide emulsion without the use of reducing agents (developers) lies in the fact that the darkening of the latter is caused by the irreversible reduction of (three-dimensional) crystals to metallic Ag particles, whereas here only a sorbed monolayer on the particle surface is available.

coalesce into only one (cubic) crystal, the latter has a length of 140 atomic diameters or 0.04μ, i.e., the cube is equivalent in size to 1/10 of a wave-length of light; it would, however, cover only 1/200 of the particle area which contributes to the albedo. If it is assumed that the Ag atoms available coalesce, e.g., at 10 centers instead of one, the resulting average crystal size will only be 1/20 of a wave-length, and these crystals will cover 1/75 of the surface of the particle, etc.

While the lack of resolvable microscopic detail on normally exposed surfaces indicates the smallness of these centers, it appears impossible to account with such minute structural changes[25] at the particle surface for the order of magnitude of the observed albedo differences between the *O*- and the *R*-state, which, e.g., for rutile, amounts to a relative albedo decrease of 80 percent and more (Fig. 5).

A possible solution for this difficulty is presented by the following assumption: The transition from the *O*- into the *R*-state initially takes place only on the exposed surfaces of the top layers of the particles, as described above. The excited silver coalesces at one or several centers on each particle; this change in surface structure, however, does not contribute appreciably to the variation of the albedo. The chemical equilibrium of the surface is, however, destroyed by this depletion, and the tendency for its reestablishment will cause a migration of Ag (or AgOH) from the surfaces of the undisturbed (not exposed) particles onto the depleted sections of the exposed particle surfaces. This migration will come from centers of Ag supply, such as free, i.e., unsorbed silver oxide particles, present in almost all samples tested (since the Ag content was above the saturation value), or from the particle surfaces below the top layer. This migration is, of course, greatly facilitated by the presence of water at the interfaces of the particles, i.e., in the state of an aqueous gel.

It is obvious that, by this process of replenishment and subsequent transformation into the *R*-state, an almost unlimited amount of Ag can be collected on the exposed surface, that is to say, enough to explain the drastic changes of optical properties on the surface. This assumption is supported by a number of observations:

First, Kohlschuetter and d'Almendra[2] report the formation of visible Ag crystals on the surface of ZnO particles suspended in a solution containing Ag ions in a very much higher concentration than in these experiments. This proves the fact, however, that Ag crystals do form on the hydrated surface of ZnO particles.

Second, the photosensitivity is largely dependent upon the presence of moisture, which latter will facilitate the transition of migration of Ag from one particle to another.

Third, as previously mentioned, an exposed area of relatively dry material darkens spontaneously over the region wetted subsequently with a drop of water.[26]

Fourth, it is noteworthy that (according to B-2) the maximum albedo variation remains unaffected by a large excess of Ag_2O as long as an excessive over-exposure is avoided; the configuration of the silver nuclei on the surface in the *R*-state is approximately the same whether or not the Ag supply comes from lower particle strata or from free Ag_2O. This is further supported by the fact that no change in photosensitivity is observed after a reversion with H_2O_2 which should reduce any Ag_2O quantitatively into Ag.

The process of the reversion of the *R*- into the former *O*-state involves, obviously, a complete redistribution of the Ag atoms from coalesced discrete nuclei into their former positions on the particle surfaces as monolayer. It must be assumed that the presence of activated oxygen causes a reaction (oxidation) with the nuclei by which the Ag atoms are set free, i.e., are converted into a reaction product of higher solubility than that of the Ag nuclei so that they are able to redistribute themselves under conditions similar to those originally present when Ag was introduced in the form of Ag_2O particles mixed with the substrate.

This assumption is supported by the dependence of the rate of reversion on the presence

[25] It has been attempted to trace the Ag on individual ZnO particles under the electron microscope, but without satisfactory results. In a few cases the appearance of dark beads on the surface of needle-shaped ZnO crystals could be observed, but the conditions of electron microscope samples are too different from the state of the photosensitive gel to permit any valid conclusions.

[26] This phenomenon, not further investigated at present, appears almost to be analogous to the latent image and its subsequent development process in an Ag-halide emulsion.

of water (reversion by H_2O_2) and on the smallness of the Ag nuclei formed, both of which aid the process of re-establishment of the *O*-state, the former by facilitating diffusion, and the latter by increasing the rate of the oxidation.

Since, on the other hand, the rate of re-oxidation should be less on larger nuclei and the size of the individual nuclei formed depends upon the magnitude of the absorbed radiation, the observed persistence of the intense mercury lines (in particular, 3650A), as well as the faster disappearance of the long-wave part of the spectrum, may be anticipated.

The relatively long duration which characterizes the reversion process in the experiments with O_3 on practically dry samples must be due to a retention of O_3 in the remaining traces of moisture which permits only a limited degree of redistribution by diffusion over the interfaces of the particles.

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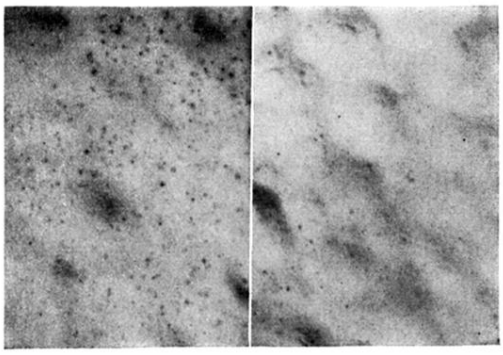
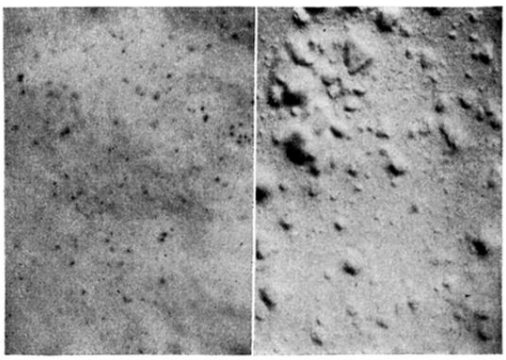


(a) (b)

FIG. 3. Photo-sensitive gel on ZnO substrate (2 percent Ag_2O) 84×, Zeiss Ultrapak dark-field illumination. (a) Immediately after homogenization. (b) After 37-hour digestion. Note the presence of free Ag_2O particles in (a) and the almost complete disappearance in (b).



(a) (b)

FIG. 4. Photo-sensitive gel on TiO_2 (anatase) substrate (2 percent Ag_2O) 84×, Zeiss Ultrapak dark-field illumination. (a) Immediately after homogenization. (b) After 37-hour digestion. Note the presence of free Ag_2O particles in (a) and the complete absence in (b).

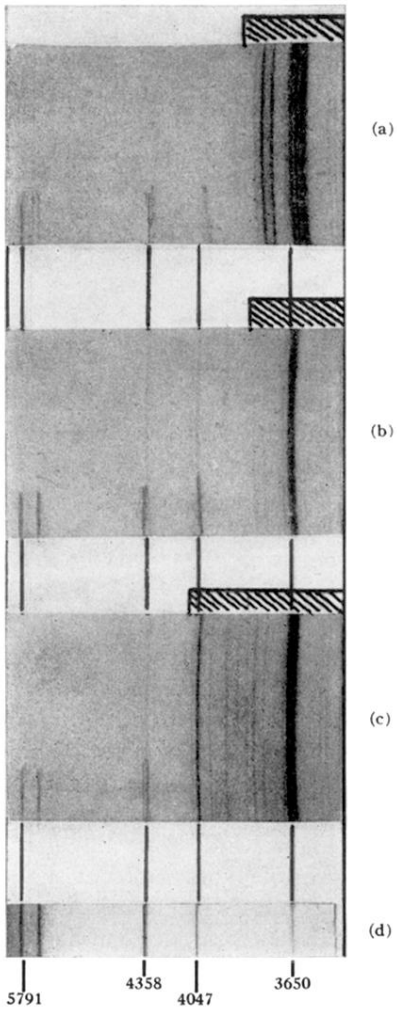


FIG. 6. Photographic reproduction of Hg-arc spectrum images (all unretouched, 2.1×magnified) on: (a) ZnO containing 1 percent Ag_2O. (b) TiO_2 as anatase containing 1 percent Ag_2O. (c) TiO_2 as rutile containing 1 percent Ag_2O. (d) Panchromatic film for comparison. The absorption bands are marked for each substrate. Since the longwave lines are very difficult to distinguish on the photographic reproduction, they are marked in the lower half of each photo.