Photo-Stability of Suspensoids[1]

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Colloidal suspensions have been shown by Young and Pingree (1) to be light-sensitive with respect to their rates of migration under electrical stress. In some cases the effect was found to be positive and in others negative.

Knowing that catalytic activity of colloidal platinum on hydrogen peroxide is destroyed by boiling, Farmer and Parker (2) in 1913 demonstrated that this activity can also be destroyed by the action of ultraviolet light.

It was pointed out by Spear (3) and his co-workers that coagulation of Bredig's platinum hydrosol was greatly accelerated by exposure to a 220 volt Cooper-Hewitt quartz lamp.

In 1929 Lal and Ganguly (4) showed that the coagulation and the accompanying change of pH of thorium hydroxide sol when exposed to the full radiation of a quartz mercury arc was due to the photochemical decomposition of the stabilizing agent, nitric acid. Similarly, the coagulation of silver in tannic acid containing a trace of potassium nitrate was explained by the photochemical decomposition of the tannic acid generating small amounts of ammonia. Their work seems to show that the coagulating effect of the rays is independent of the sign of the colloids; the oppositely charged sols coagulate at about the same rate, increasing the pH in the case of negatively charged colloids and decreasing it in the case of positively charged colloids. It was suggested that the coagulation of colloidal solutions by light is due to the chemical and photochemical decomposition of the stabilizing electrolytes.

Emulsions of benzene, benzine, and carbon disulfide in water, with sodium oleate as emulsifying agent, were separated into two layers on exposure to ultraviolet light, and this was accompanied by an increase in pH. Sinha and Ganguly (5), who studied this, indicated that the layer-breaking was partially due to the destruction of the emulsifying agent by ultraviolet radiation.

Following up the earlier work on the effect of sunlight on numerous sols, Dhar and Roy (6) and Shella (7) concluded that sols can be grouped into two classes: (a) those like iron, chromium, tellurium, aluminum, tin, and thorium hydroxides, prepared in a hot condition, and vanadium pentoxide, manganese dioxide, and mercuric sulfide, all of which are rendered unstable toward electrolytes after exposure; and (b) those like Prussian blue, copper ferrocyanide, gum dammar, and mastic, which become stabilized in the presence of electrolytes. Certain sols were coagulated by sunlight and were found to have a higher conductivity than those in the dark. The coagulation by light is thought to be due to the decomposition of the stabilizing ions and the loss of reactivity of the particles of the sols. On the analysis of the absorption

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spectra of exposed and unexposed sols there was found to be a marked absorption in the case of arsenic trisulfide, Prussian blue, and ferric hydroxide, while gum dammar and mastic showed less disintegration on exposure to light.

In this investigation the influence of radiation of various wave-lengths on the stability of both hydrosols and organosols with respect to the effect on particle size, pH, and change on photochemical reactions are studied.

Experimental

Materials.—All the chemical reagents used in the preparation of colloidal suspensions were of C. P. quality.

The methyl, ethyl, and n-propyl alcohols were all refluxed over quick-lime for several hours and then distilled. The middle portion of the distillate was again refluxed over a small amount of lime for 10 hours before again redistilling.

The benzene used was made anhydrous and thiophene-free by shaking with concentrated sulfuric acid. This process was repeated three times, after which the benzene was distilled in the presence of calcium chloride. The middle fraction was collected for use.

The acetone used was purified according to the method of Shipsey and Werner **(8)**.

Apparatus.—The source of ultraviolet light used in this investigation was a Cooper-Hewitt lamp of the quartz mercury vapor type manufactured by the General Electric Vapor Lamp Company of Hoboken, New Jersey. It operated on a 110 volt D. C. line, using 2.5 amperes with a fall of potential across the arc of 15 volts. The lamp, equipped with an enamelled reflector, was placed in the upper part of an asbestos lined box of the dimensions 12″ x 12″ x 16″. Inside this box or reaction chamber were placed water coils to maintain the temperature at about 28° C. In some cases a filter, No. 980 Red Purple Corex "A", of 3.5 mm. thickness, made by the Corning Glass Company, was used to filter out other wave-lengths, thus transmitting only wave-lengths from 2500 Å to 4000 Å.

The intensity of ultraviolet radiation from the lamp was measured according to the method described by Anderson and Robinson **(9)**. In five hours, 37.8 mg. of oxalic acid were decomposed, or 3.91×10^5 ergs per second were required to decompose 1 mg. of oxalic acid in 30 minutes.

The infrared and visible radiations were obtained from a Thermo-Ray lamp built by the McIntosh Electrical Corporation of Chicago. It was equipped with a 1000-watt tungsten filament and nitrogen-filled bulb, Luchiesh, M. **(10)**. This lamp was placed in the upper compartment of a large wooden box. In the shelf which divided the upper compartment from the lower, was fitted a light filter, Sextant Red, 6″ x 6″ and 3.5 mm. thick, manufactured by the Corning Glass Company. Thus the box served a dual purpose. The upper compartment was used for visible light which, when passed through the filter into the lower compartment, gave infrared rays of the wave-lengths 8000 Å to 10,000 Å.

Preparation of Colloidal Suspensions.—Bismuth hydroxide hydrosol was prepared by adding with constant stirring 150 ml. of concentrated ammonium hydroxide to 300 ml. N/10 bismuth nitrate. The bismuth hydroxide, when washed free of basic salt by centrifuging and subsequent decantation, becomes dispersed in pure water. The concentration of the sol was 1.8 grams per liter.

Aluminum hydroxide hydrosol was prepared by precipitating 5.78 g. of aluminum chloride hexahydrate in 200 ml. of water with ammonium hydroxide. The precipitate was washed with hot water and transferred to a flask containing 500 ml. of water, to which was added just enough N/20 hydrochloric acid to bring about peptization. The suspension was then heated to boiling.

Arsenious sulfide hydrosol was prepared by diluting 200 ml. of a cold saturated solution of arsenious oxide to 400 ml. and adding it slowly to a solution made by saturating 2 ml. of water with hydrogen sulfide which was then diluted to 200 ml. The mixture was then diluted to two liters with a hydrogen sulfide solution ten times as strong. The whole was then treated with hydrogen sulfide gas until completely saturated. The resulting yellow sol was then divided into two portions, one of which was subjected to boiling to remove the excess hydrogen sulfide and marked *Sol 1*. The other portion was treated with hydrogen gas to remove the excess hydrogen sulfide and marked *Sol 2*. The concentration of these sols was found to be 18.7 g. arsenic trifulfide per liter.

Cadmium sulfide hydrosol was prepared by precipitating cadmium sulfide by adding ammonium sulfide solution to cadmium nitrate solution. The precipitate was washed free of excess ammonium sulfide. Suspension was brought about by bubbling hydrogen sulfide, which has a peptizing action, through the solution **(11)**. The excess hydrogen sulfide was removed by passing hydrogen gas through the suspension. The concentration of the resulting hydrosol was found to be 2.7 g. per liter.

Antimony sulfide hydrosol was made by passing hydrogen sulfide gas through a solution of 5 g. potassium antimony tartrate in one liter of water. The resulting suspension was dialyzed for three days at room temperature.

Zinc sulfide hydrosol was formed by passing hydrogen sulfide gas into water containing in suspension pure zinc hydroxide, which was previously precipitated by ammonium hydroxide from the chloride salt according to the method of Taylor **(12)**.

Sulfur hydrosol was prepared in the usual manner by passing hydrogen sulfide gas into water saturated with sulfur dioxide.

Mercuric sulfide n-propyl alcosol was prepared by pouring slowly a solution of 0.75 g. of mercuric cyanide into 250 ml. of n-propyl alcohol saturated with hydrogen sulfide. A deep brown sol formed immediately and turned black rapidly. Dry hydrogen gas was then passed through the sol for 24 hours, removing the excess hydrogen sulfide (Weiser and Mack, 13). The concentration was found to be 1.0 g. per liter.

Mercuric sulfide ethyl alcosol was prepared by disolving mercuric cyanide in absolute alcohol and treating with dry hydrogen sulfide gas,

(Errera, **14**). The resulting alcosol contained 2.5 g. mercuric sulfide per liter.

Mercuric sulfide sol in acetone was prepared in the same manner as mercuric sulfide ethyl alcosol.

Copper sulfide ethyl alcosol was prepared in a manner similar to that used in preparing the mercuric sulfide, using copper acetate. The resulting suspension was found to contain 37 g. cupric sulfide per liter.

Arsenious sulfide sol in nitrobenzene was prepared in the way described by Galt (**15**).

Sulfur sol in benzene was prepared in a manner similar to that used by Bikerman (**16**). The resulting sol contained 0.6% sulfur.

Suspensions of magnesium, barium, and calcium carbonates in ethyl alcohol were prepared according to the method outlined by A. van Busbagh (**17, 18**). The concentration of these sols was found to be about ten grams per liter.

A 2% suspension of sodium caseinate was prepared and used as the casein hydrosol.

Purified Chinese egg albumin was used in preparing the albumin suspension. Ten grams were suspended in 500 ml. of water.

Ash-free gelatin was prepared according to the improved method described by Loeb (**19**).

Soybean protein, containing mostly glycinin, was prepared in exactly the same manner as the casein hydrosol mentioned above.

Procedure.—Fifteen-ml. portions of the sols were exposed to the different radiations for a definite period of time in quartz flasks (ultraviolet), small crystallizing dishes (infra-red), and specially-blown thin-walled glass flasks (visible). The sols were kept at a distance of 15 mm. from the source of light in all cases. A similar portion of the same sol was kept in a dark chamber at about the same temperature for comparison.

The pH of the clear or nearly clear supernatant liquid of the sols which had been coagulated by light was determined and this value compared with the pH of clear sols obtained by centrifuging the sols (2200 R. P. M.) of shorter radiation periods or no radiation (in dark). The hydrogen electrode was used for the alkaline suspension and the quinhydrone electrode for the acid protein solutions. The Helige colorimetric comparator was used for some of the emulsoids. The effect of radiations on pH of the suspensions is given in Table I.

In order to determine the coagulating power of different electrolytes, a measured volume of the sol was placed into a clean graduated test tube and made up to 5 ml. while a known amount of a standard solution of an electrolyte was placed into another tube and was also made up to 5 ml. The two solutions were then carefully mixed, and one hour later coagulation was noted. The liminal values of electrolyte concentration were determined according to Thomas (**22**). The results are expressed as ml. of electrolyte which must be diluted to 5 ml. in order to bring about coagulation in one hour and are recorded in Table II.

Discussion of Results

Aluminum hydroxide sol was completely coagulated in 24 hours under visible and infrared radiation and in 22 hours under ultraviolet.

Both arsenious sulfide hydrosols were completely coagulated in six hours, with the exception of those exposed to infrared rays, which took 52 hours before any settling was noticed. The sols first became turbid but retained their original color. Later the sols appeared partly precipitated, but the supernatant liquid was still pale yellowish white. Finally the sols precipitated completely, leaving a clear liquid and a mass of free sulfur particles settling on the bottom of the dish. Under infrared rays there was no apparent change except on prolonged exposure, when a small amount of free sulfur settled on the dish. The antimony, cadmium, and zinc sulfides showed about the same changes as arsenic trisulfide at first except that the red-orange color of the antimony trisulfide became orange and the cadmium sulfide coagulated more rapidly, leaving the supernatant liquid clear. The increase in particle size of these sols on exposure was easily observed by means of the Tyndall

TABLE I.—Effect of Radiations on pH of Suspensions

SOL	Time of Exposure (hours)	pH				
		Ultraviolet		Visible	Infrared	Absence of light
Bismuth Hydroxide	2	6.60		6.51	6.50	6.42
	4	6.69		6.60	6.56	
	8	6.80		6.70	6.62	
	10	6.81		6.72	6.66	
Aluminum Hydroxide	2	6.54		6.46	6.42	6.35
	4	6.63		6.53	6.47	
	8	6.67		6.58	6.50	
	12	6.66		6.60	6.51	
Arsenious Sulfide Sol 1	0.5	3.78	3.93*	4.07	——	4.38
	1	3.54	3.73	3.91	4.55	
	2	3.35	3.58	3.85	4.72	
	4	3.20	3.42	——	——	
	5	——	——	3.83	4.90	
	6	3.11	3.42	——	——	
	8	2.90	——	——	5.13	
	9	——	3.40	——	——	
	10	2.88	——	3.76	5.22	
Arsenious Sulfide Sol 2	1	3.67	4.05	——	——	4.45
	2	3.32	3.64	3.95	——	
	3	——	——	——	5.05	
	4	3.10	3.40	——	——	
	5	——	——	3.82	——	
	6	2.95	3.31	——	5.26	
	8	2.89	3.30	——	——	
	10	2.80	3.30	3.77	5.36	
Cadmium Sulfide	1	3.18		3.25	3.20	3.55
	2	3.05		3.15	——	
	4	3.00		3.14	3.12	
	7	2.88		3.10	3.06	
Antimony Sulfide	1	3.80		——	——	4.05
	2	3.64		3.90	4.10	
	4	3.43		——	——	
	5	——		3.83	4.14	
	6	3.24		——	——	
	8	3.15		——	——	
	10	3.08		3.77	4.17	

*Ultraviolet light used with filter in the experiments reported in this column.

TABLE I.—Effect of Radiation on pH of Suspension—Continued

SOL	Time of Exposure (hours)	pH			
		Ultraviolet	Visible	Infrared	Absence of light
Zinc Sulfide	1	3.60	3.58	3.55	3.85
	2	3.45	3.45	3.43	
	4	3.32	3.40	3.39	
	8	3.30	3.39	3.38	
	10	3.30	3.38	3.32	
ORGANOSOLS					
Mercuric Sulfide n- propyl alcosol	5	4.87	4.91	5.00	5.28
	10	4.78	4.82	4.87	
	15	4.74	4.78	4.81	
Mercuric Sulfide ethyl alcosol	5	4.83	4.89	4.92	5.30
	10	4.72	4.76	4.79	
	15	4.68	4.70	4.75	
Mercuric Sulfide in acetone	10	2.86	2.47	2.53	3.25
Copper Sulfide ethyl alcosol	5	3.38	3.47	3.58	3.92
	10	3.25	3.35	3.39	
	15	3.21	3.24	3.30	
Magnesium Carbonate ethyl alcosol	10	7.51	7.98	7.76	7.05
	20	7.82	8.19	8.10	
	30	8.06	8.20	8.10	
Barium Carbonate ethyl alcosol	10	7.55	8.02	7.70	6.98
	20	7.93	8.20	8.05	
	30	8.10	8.20	8.15	
Calcium Carbonate ethyl alcosol	10	7.37	7.80	7.65	7.08
	20	7.43	8.05	7.94	
	30	8.00	8.10	8.04	
Sodium Caseinate	4	7.35	7.42	7.44	7.64
	8	7.24	7.30	7.37	
	12	7.20	7.25	7.28	
Egg Albumin	2	7.60	7.62	7.63	7.83
	4	7.52	7.55	7.59	
	8	7.43	7.46	7.50	
	12	7.38	7.40	7.46	
Gelatin	5	7.73	7.63	7.85	7.90
	10	7.56	7.54	7.63	
	20	7.49	7.50	7.58	
	30	7.44	7.47	7.55	
Glycinin	5	7.45	7.30	7.35	7.56
	8	7.28	7.25	7.22	
	10	7.25	7.18	7.20	

effect. The yellowish beam became reddish with the increase in particle size due to prolonged exposure.

Sulfur sol is so sensitive to light that it coagulated completely in half an hour exposure to all wave-lengths.

The zinc sulfide hydrosol coagulated in 35 hours under visible rays, 29 hours under ultraviolet, and 38 hours under infrared radiation.

The mercuric sulfide ethyl alcosol coagulated in 55 hours under visible, 58 hours under infrared, and 38 hours under ultraviolet.

Sulfur suspended in benzene did not coagulate in 15 hours.

The results in the preceding tables show that the basic protein sols of casein, egg albumin, gelatin, and glycinin under the influence of light

TABLE II.—Coagulation by Electrolytes

SOL	Electrolyte	Expos. (Hours)	Ml. electrolyte required to produce coagulation in 1 hour			
			Ultra-violet	Visible	Infrared	No exposure
HYDROSOLS						
Bismuth, hydroxide	N KCl	4	2.55	2.60	3.62	2.84
	N/10 Na_2SO_4	8	3.07	3.12	3.15	3.25
Zinc, sulfide	N KCl	8	2.15	2.20	2.25	2.58
	N/10 Na_2SO_4	8	3.32	3.40	3.37	3.65
	N/13 $FeCl_3$	8	1.85	1.90	2.00	2.20
ORGANOSOLS						
Mercuric, sulfide, n-propyl, alcosol	N/10 KCl	5	2.05	2.18	2.08	2.15
	N/10 LiCl	5	1.57	1.52	1.60	1.50
	N/10 KCl	10	2.00	2.15	2.20	——
	N/10 LiCl	10	1.45	1.50	1.55	——
Mercuric, sulfide, ethyl, alcosol	N/10 KCl	5	3.45	3.56	3.55	3.64
	N/10 LiCl	5	1.46	1.52	1.50	1.65
	N/10 KCl	15	3.40	3.45	3.50	——
	N/10 LiCl	15	1.40	1.47	1.43	——
Mercuric, sulfide in acetone	N/50 LiCl	10	2.32	3.15	2.30	2.45
Copper, sulfide, ethyl, alcosol	N/10 KCl	5	3.95	4.00	4.50	4.84
	N/10 LiCl	5	1.80	1.85	1.88	2.05
	N/10 KCl	15	3.90	3.95	4.20	——
	N/10 LiCl	15	1.67	1.79	1.70	——
Magnesium, carbonate, ethyl, alcosol	N/10 LiCl	10	0.42	0.35	0.42	0.75
	N/10 LiCl	15	0.40	0.30	0.32	——
	N/100 $NaC_2H_3O_2$	10	1.37	1.15	1.22	1.75
	N/100 $NaC_2H_3O_2$	15	1.29	1.10	1.20	——
Barium, carbonate, ethyl, alcosol	N/10 LiCl	10	0.35	0.33	0.38	0.68
	N/10 LiCl	15	0.23	0.30	0.32	——
	N/100 $NaC_2H_3O_2$	10	1.40	1.25	1.33	1.60
	N/100 $NaC_2H_3O_2$	15	1.35	1.30	1.32	——
Calcium, carbonate, ethyl, alcosol	N/10 LiCl	10	0.35	0.24	0.30	0.80
	N/100 $NaC_2H_3O_2$	10	1.42	1.25	1.30	1.72
PROTEIN SOLS						
Casein sol	N/13 $FeCl_3$	8	2.17	2.22	2.28	2.34
Albumin sol	N/13 $FeCl_3$	8	2.38	2.44	2.40	2.65
Gelatin sol	N/13 $FeCl_3$	8	2.95	2.84	2.87	3.15
Glycinin sol	N/13 $FeCl_3$	8	2.20	2.32	2.25	2.85

rays become unstable toward electrolytes when near a pH of 7 after prolonged exposure.

Conclusions

In general the experimental results give credence to the theory that radiations over a wide range of wave-lengths have a decided influence on the stability of colloids, both hydrosols and organosols. This effect, according to Charem **(20)** and Slintizing **(21)**, is not solely a physical process but a photo-activated chemical change in either the dispersion medium or the stabilizing ions present.

The pH changes are credited to the chemical reactions induced by radiation on these sols. The increase in pH in the case of hydroxide hydrosols was due to the photo-chemical decomposition of small quantities of acid, especially nitric, which remains in the colloidal system as a stabilizing agent. The decomposition of the acid thus rendered the colloids less stable than before exposure.

In an analogous manner the decomposition of carbonic acid to carbon dioxide by various radiations of light accounts for the increase in pH of the alkaline carbonate alcosols. Consequently, the unexpected results of the pH of the arsenic trisulfide hydrosols after exposure to infrared rays may be due to the decomposition, rather than the oxidation, of the hydrogen sulfide which is present in small amounts.

On the other hand, the pH values of sulfide hydrosols and organosols, particularly the arsenic trisulfide and antimony trisulfide under visible and ultraviolet radiations, were decreased. This is probably due to the oxidation of a trace of hydrogen sulfide (which is present in the colloidal system as a stabilizing ion adsorbed on the surface of the colloidal micelles) to thionic acids by the radiations. On further exposure a secondary reaction may occur between the hydrogen sulfide and its oxidation products which would produce sulfur in small amounts. This colloidal sulfur might remain suspended for a time, but as exposure was continued, more sulfur would precipitate and the suspension finally settle when the concentration of sulfur became sufficiently large.

The organosols were more difficultly coagulated by various radiations due to the fact that there is an insufficient amount of water present to bring about the oxidation of the hydrogen sulfide present in the system.

Since the influence on the stability of lyophobic colloids and organosols can be accounted for, at least quantitatively, by considering the effect upon the dielectric constant of the medium, on the ionization of the electrolytes present, and on the selective adsorption of ions by the colloidal micelles, it is not to be expected that the organosols would behave in the same way toward light as the corresponding hydrosol would. In fact, the hydrosols themselves are governed to some extent by the above factors. However, the sols of both these classes become unstable toward electrolytes and can be coagulated by subjecting to radiations of various wave-lengths. It is evident that the light-rays can act by photochemical means to disturb or destroy the stabilizing ions adsorbed on the surface of the colloid micelles, thus bringing about instability and subsequent coagulation of the colloids.

It may be seen from Table II that all colloids studied became less stable toward electrolytes on prolonged exposure to all wave-lengths used in this investigation. This is to be expected if light rays actually disturb the adsorbed stabilizing ions.

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