Three distinct addition compounds are indicated by the curve: $H_2O \cdot HF$, $H_2O \cdot 2HF$ and $H_2O \cdot 4HF$. The second does not quite melt congruently, but the shape of the curve hardly leaves any doubt that it has the composition given. The first of these has been prepared by Metzner[4] by freezing it from hydrofluoric acid solutions. He reports its melting point to be $-35°$, which is not far from our value, $-35.4°$.

Before anything very definite can be said concerning the configuration of these compounds, it will be desirable to have data bearing upon their crystal structures. We will merely call attention to the fact that the observations of Berliner and Hann[2] are extended by the discovery of the compound $H_2O \cdot 4HF$ and that the existence of two compounds with an excess of HF, while there are none with an excess of H_2O, harmonizes with the view that HF tends to assume a more complex polymerization than water.

Summary

The freezing point–composition diagram for the system water–hydrogen fluoride has been studied over the entire range. In addition to the solid compound $H_2O \cdot HF$, previously known, we have discovered the compounds $H_2O \cdot 2HF$ and $H_2O \cdot 4HF$.

BERKELEY, CALIFORNIA

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MEASUREMENTS OF THE FLUORESCENCE OF CELLULOSE ACETATE, CELLULOSE NITRATE AND GELATIN IN ULTRAVIOLET LIGHT

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The fluorescence of cellulose in ultraviolet light was first noted by Hartley[1] in 1893 but no further attention seems to have been given the subject until Judd-Lewis began a series of experiments in 1918. In his first communication, Judd-Lewis[2] described the appearance of various cellulosic derivatives when held where the photographic plate is normally placed in a quartz spectrograph. Cellulose acetate, viscose, filter paper and "normal" paper showed strong fluorescence in the ultraviolet region while nitrocellulose and paper treated with ethyl malonate showed very little fluorescence.

A method of photographing the fluorescent spectrum was devised by this author[3] in which a camera was mounted in the back of the spectrograph arm and the spectrum photographed by reflected light, a procedure necessi-

[1] W. N. Hartley, *J. Chem. Soc.*, **63**, 243 (1893).

[2] S. Judd-Lewis, *J. Soc. Dyers Colourists*, **34**, 167 (1918).

[3] S. Judd-Lewis, *ibid.*, **37**, 201 (1921).

tated by the opacity of the materials under investigation. The densities of the spectral lines obtained on the plate were compared with the corresponding lines of an arbitrarily chosen standard paper, the specifications for which are not given. It is not possible, therefore, for other workers to compare their results with those of Judd-Lewis, but a qualitative idea of some of his results may be gained. Various types of filter paper were found to give divergent results and no relation was observed to exist between the fluorescent power and any other property of the paper. It was certain, however, that moisture content had little to do with the phenomenon. The fluorescence of hydrocellulose increased markedly as the period of time the pulp was left in the beater increased, the most rapid rate of change taking place in the interval between two and three hours' beating. This might be taken to mean that ultraviolet fluorescence increases as the molecular degradation of cellulose proceeds, which cannot be true without limits because the ultraviolet fluorescence of glucose is less intense than that of cellulose.

In the last papers by Judd-Lewis[4] a description was given of the fluorescent spectrum of a large number of cellulose products examined in a tungsten arc lamp. It was shown that fluorescence was excited by all the wave lengths present below $\lambda 330$ mμ. The physical condition of the specimen seemed to play no part in determining the fluorescent spectrum, as a comparison of data obtained with the same cellulose acetate in the form of a powder, a paper and a transparent film showed little if any difference. The fluorescence did appear to be sensitive to slight chemical changes, as cellulose, hydrocellulose and oxycellulose could be easily distinguished by this means.

Pringsheim and Gerngross[5] have reported that the fluorescence in ultraviolet light of a number of organic polymers—lichenin, cellulose, glycogen, inulin, acetate, gelatin, etc.—increased as the colloidal material was disgregated. The observations were made visually and it was suggested that this property of organic colloidal materials in general might be used to characterize their state of aggregation.

Data of a conflicting nature were obtained by the present authors while attempting to use this property of cellulose acetate to indicate something about the micellar structure of the material. Visual evidence was obtained that the physical structure of the substance was related to its fluorescent power and that marked changes in colloidal properties might be accompanied by no variation in fluorescent properties. The quantitative experiments described in this paper were carried out to determine what relation, if any, existed between the physical and colloidal structure and fluorescent properties of cellulose acetate and cellulose nitrate and gelatin.

[4] S. Judd-Lewis, *J. Soc. Dyers Colourists*, **38**, 99 (1922); **40**, 29 (1924).

[5] H. Pringsheim, and O. Gerngross, *Ber.*, **61**, 2009 (1928).

The Fluorescence of Cellulose Acetate and Cellulose Nitrate Films

Method of Measurement.—When the image of a mercury arc spectrum is focused on a film of cellulose acetate, the lines of the spectrum are visible in a dark room down to λ241 mμ. The region from λ241 mμ to 365 mμ is so far below the limit of visual perception that no question exists but that the visible light is fluorescent light excited by the ultraviolet. The fluorescent radiation is gray-blue in color and the color is independent of the frequency of the exciting radiation. The fluorescence is not polarized and is passed with high intensity by the K2 Wratten filter but is almost completely absorbed by the K3 filter, which fact places the wave length of the light emitted as between λ485 mμ and 505 mμ, the limits for 60% transmission for the K2 and the K3 filters, respectively.

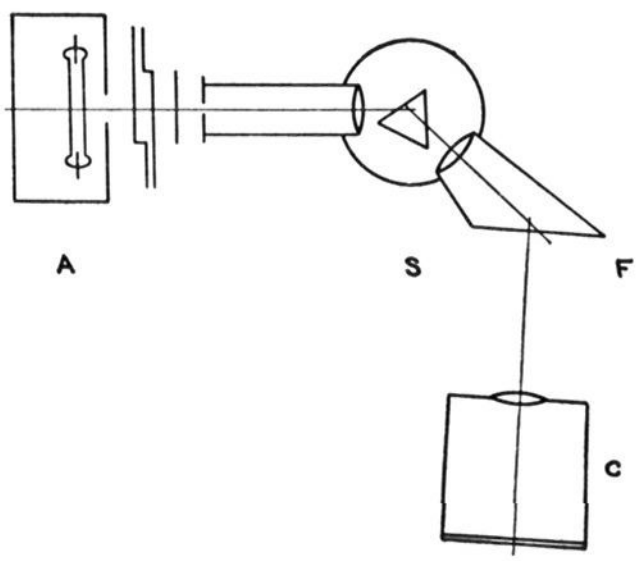

Fig. 1.—Apparatus for measuring fluorescence in films.

The apparatus used to record the fluorescent light emitted by the cellulose acetate films is indicated by the diagram in Fig. 1. Light from the Cooper-Hewitt quartz mercury arc A was resolved by the Gaertner quartz spectrograph S and images of the slit formed on the film under investigation at F. The fluorescent image was photographed by the camera C. The lamp was operated at 155 volts. Using an f 4.5 lens in the camera and Eastman Speedway plates, a suitable time of exposure was found to be forty minutes. The plates were all developed in metol–hydroquinone process developer to a gamma of one.

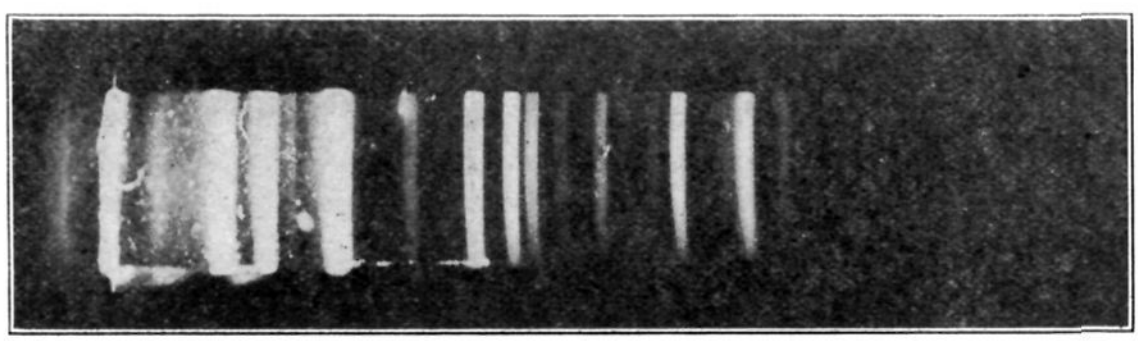

Fig. 2.—Fluorescence of cellulose acetate in the mercury arc spectrum.

Figure 2 is a photograph of the fluorescent light excited by ultraviolet radiations falling on afilm of cellulose acetate. To compare the fluores-

cence of different samples, the densities of the lines in this plate were measured by a micro-densitometer and compared with the densities of the lines obtained by making a direct photograph of the ultraviolet spectrum by placing the photographic plate at F, the time of exposure being one-tenth of a second. The ratio density of fluorescent line to density of spectral line was plotted against the wave length of the exciting radiation. This ratio approaches proportionality to intensity of fluorescent light/intensity of incident light so long as the exposures are low, but as either or both exposures increase, it becomes more nearly proportional to $(P_1 \log I_1)/(P_2 \log I_2)$ where P_1 and P_2 are the Schwarzschild coefficients for the respective wave lengths of fluorescent and incident light. This ratio will be noted hereafter as R.

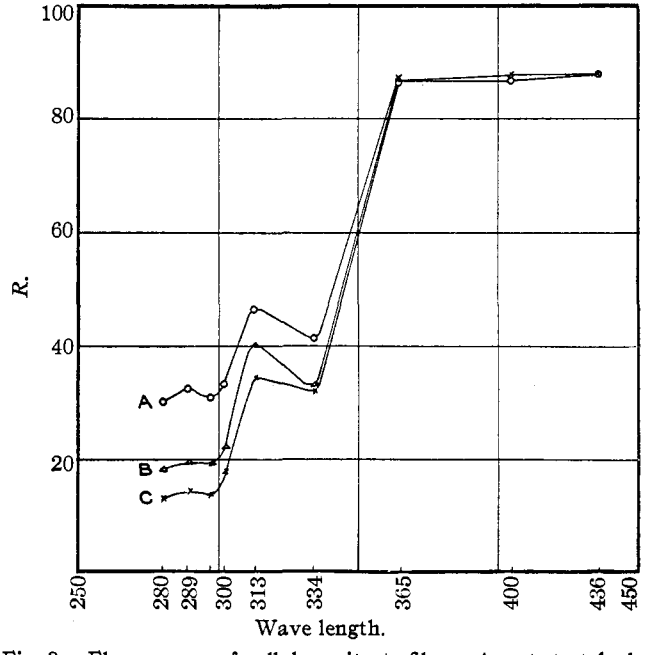

Fig. 3.—Fluorescence of cellulose nitrate films: A, not stretched; B and C, stretched.

Relation between Structure and Fluorescence in Cellulose Nitrate Films.—The curves shown in Fig. 3 were constructed in the manner indicated above and show the fluorescence of three sheets of cellulose nitrate film prepared from the same solution of the original cellulose nitrate. It is evident from the figure that in the region of λ280 to 334 mμ there exists a marked difference in the fluorescent powers of the films forming the order A, B, C, in their ability to fluoresce in this spectral region. The film that showed the fluorescence described by Curve A was formed by evaporating

the cellulose nitrate dope to dryness on a glass plate. The other two films were removed from the plate on which the dope was coated while they still contained about 15% of solvent and were further cured while held under tension from two ends, the film represented by Curve C being under higher tension than the film B. It has been shown by one of the present authors and S. E. Sheppard[6] that the tensions on a colloidal film during drying alter the micellar orientation of the film to such an extent that films may be prepared showing the typical optical properties of different crystallographic systems. The film A behaves optically as a section of a uniaxial crystal cut

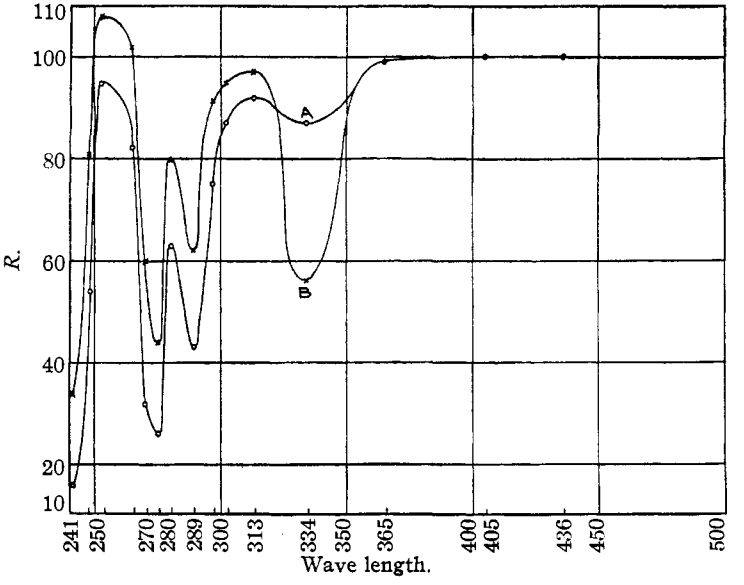

Fig. 4.—Fluorescence of cellulose tri- and diacetate films: A, cellulose triacetate; B, cellulose diacetate.

perpendicular to the optical axis while the films B and C behave as biaxial films, C being more highly anisotropic than B. It has been shown that the micellar orientation of the film[6] determines its optical properties and it must now be concluded that the ultraviolet fluorescence of the film is also related to its micellar structure.

Fluorescence in Cellulose Acetate Films.—Before proceeding with an examination of the fluorescence of a large number of cellulose acetate films, it was first ascertained that variations in the thickness of the film within wider limits than encountered with our specimens produced very little change in the photograph of the fluorescent light. A comparison of the fluorescence of two films of the same material, one 0.16 mm. thick and the

[6] J. G. McNally and S. E. Sheppard, *J. Phys. Chem.*, **34**, 165 (1930).

other 0.08 mm. thick, showed a difference in the R ratio of less than 3% at any value for λ.

The fluorescence excited on cellulose triacetate and diacetate films show points of similarity and of difference. In Fig. 4 the curve A represents the fluorescence of a chloroform-soluble triacetate while B was obtained from an acetone-soluble diacetate, both films being optically uniaxial. The two curves have the same general shape but the fluorescence of the diacetate falls below that of the triacetate at λ334 mμ. The curves in Fig. 5 show that this change in fluorescence is a progressive one as a triacetate is

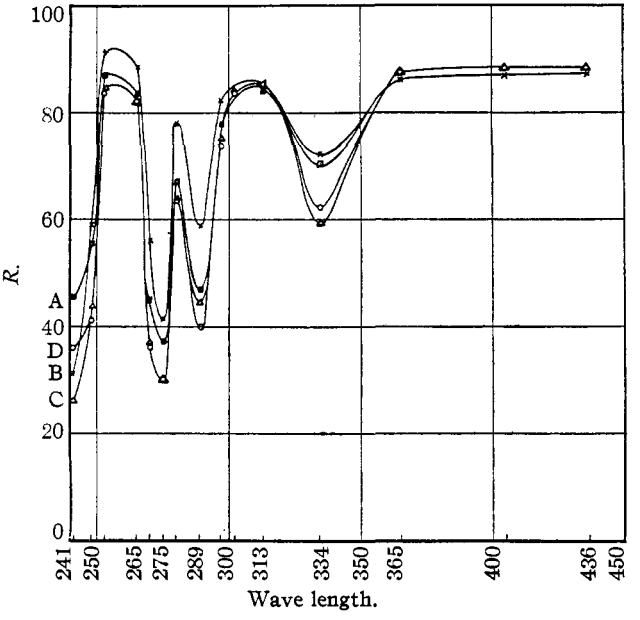

Fig. 5.—Fluorescence of cellulose acetate films of different acetyl content.

hydrolyzed to a diacetate. The data plotted in this figure were taken from samples obtained during an acid hydrolysis of a first stage dope, the samples A, B and C having acetyl values of 40, 37 and 35% and acetone viscosities of 50, 75 and 200 seconds, respectively. By milder treatment in acetylation and second stage hydrolysis, cellulose acetates may be prepared with the same acetyl values as any of the above samples but having higher acetone viscosities. The film D was made from an acetate prepared under such conditions; its acetyl value was 41% and acetone viscosity 600 seconds. When the fluorescence curve for this film is compared with the others in Fig. 5, it is seen more closely to resemble the acetate with the nearest acetyl content rather than the one most closely like it in viscosity, indicating that the chemical constitution, that is, the percentage acetyl-

ation, is a more important factor in determining the fluorescence of the material in ultraviolet light than any loosening of secondary valency forces caused by the second stage hydrolysis, or eventual depolymerization.

Divergent results were obtained when the fluorescences of stretched and unstretched films were compared in the case of two different acetates. In Fig. 6 the data show that the stretched film B fluoresces more strongly than the unstretched film A and the difference is particularly marked in the region of λ334 mμ. The data from the second acetate plotted in Fig. 7 indicate that in this case the unstretched film A is more strongly fluorescent

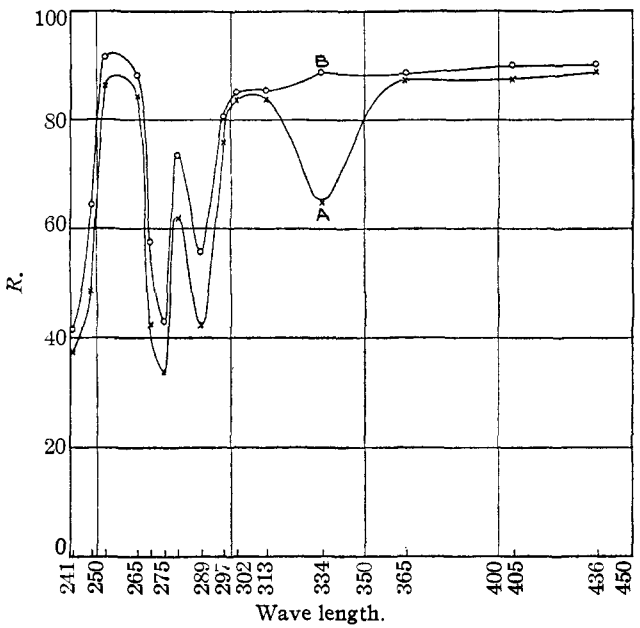

Fig. 6.—Fluorescence of cellulose acetate films: A, not stretched; B, stretched.

than the stretched film B and here the difference is most pronounced from λ265 mμ to 300 mμ. The two acetates were typically the same, having similar viscosities and both approximating the acetyl content required for a diacetate. We know of no difference in the properties of the two materials that would account for this difference in their fluorescent power..

Fluorescence in Solutions of Cellulose Acetate.—In a well darkened room, solutions of cellulose acetate can be seen to fluoresce when irradiated by ultraviolet light. The fluorescence can be observed to increase in intensity as the concentration of cellulose acetate in the solution increases; but even in the case of a 15% solution, we were unable to photograph the spectrum of the fluorescent light by means of a Gaertner quartz spectrograph after four hours' exposure. We have, therefore, excited fluorescence

in the solutions by monochromatic radiation and measured the fluorescent light given off. Figure 8 is a diagram of the apparatus used for this purpose. Light from the quartz mercury arc lamp A passed through the

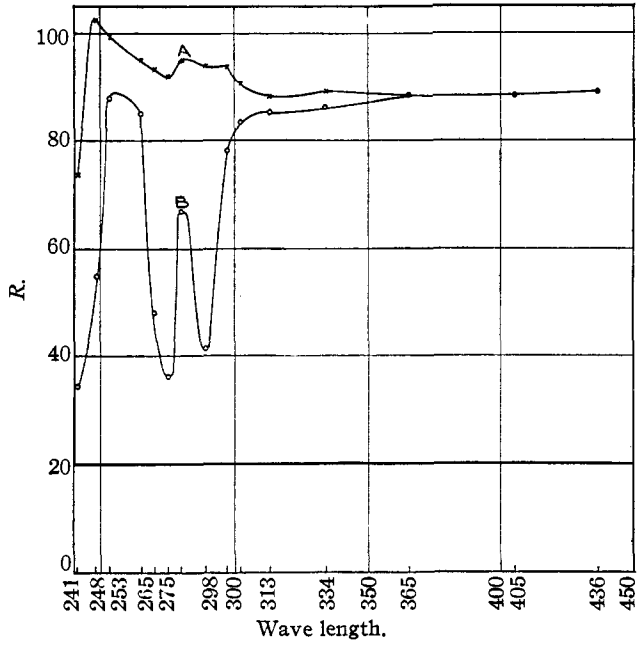

Fig. 7.—Fluorescence of cellulose acetate films: A, not stretched; B, stretched.

quartz windowed water cell W, and 18A Wratten filter, F, and illuminated the slit S_1 of a Bausch and Lomb quartz monochromator, the optical parts of which are indicated by the lenses L_1, L_2 and the prism P. The solution

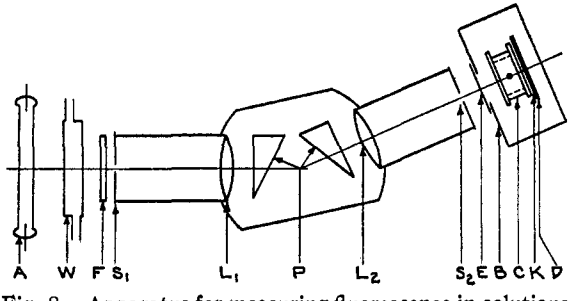

Fig. 8.—Apparatus for measuring fluorescence in solutions.

being investigated was placed in an 11-mm. quartz absorption cell C which was enclosed in a light-proof box B. The shutter E opened adjacent to the monochromator slit S_2. The Wratten filter K2 and the photographic plate

D were placed in contact with the side of the cell away from the slit. The K2 filter was found to absorb the ultraviolet light completely and transmit the fluorescent light in the case of the solutions used as well as the solid film.[7] Satisfactory plates were obtained with a 15% gelatin solution after a forty-five minutes' exposure, the plates being developed as before to a gamma of one. The densities of the plates were measured by means of the densitometer described by Capstaff[8] and the fluorescent power of the solutions compared on this basis.

The fluorescence of 15% acetone solutions of four cellulose acetates differing in their properties by very wide limits was determined by the method outlined above and the data obtained assembled in Table I. The figures in the first line refer to ball drop viscosity tests. The next line gives the percentage of acetyl group combined, and the final one, the density of the photograph of the fluorescent light after forty-five-minutes' exposure.

TABLE I

THE FLUORESCENCE OF CELLULOSE ACETATE SOLUTIONS

Sample no.	A	B	C	D
Viscosity	500	20	20	8
Acetyl, %	40	40	37.8	37.5
Density	0.36	0.40	0.42	0.42

From a consideration of the above data it appears that there is no relation between the state of aggregation of the micelles in a cellulose acetate solution and their fluorescence in ultraviolet light of wave length 365 mμ.

The Fluorescence of Gelatin Solutions.—The circumstance that films made from partially broken down gelatin are so brittle that they cannot be handled conveniently makes it a matter of great difficulty to investigate the relation between fluorescence and state of polymerization in gelatin film. We have, however, made such a study of gelatin sols using the same procedure that was outlined for use with the cellulose acetate sols.

A 10% solution of de-ashed gelatin was made up having a P_H of 5.2. The flask containing this solution was fitted with a reflux condenser and the solution boiled for twenty-four hours. Samples were taken from time to time and measurements made of the viscosity and fluorescence of the solution. Table II is a summary of these results, the density being, as before, the photographic density caused by the fluorescent light on forty-five-minutes' exposure. The viscosity measurements were made by Dr. Robert Houck and are reported in centipoise units at 40°.

[7] Aesculin and a number of glass filters were substituted for the K2 but while they had the proper adsorption limits, they fluoresced to a considerable extent in ultraviolet light and were unsuitable for the purpose at hand. No satisfactory substitute was found for the K2 filter.

[8] J. G. Capstaff, *Trans. Soc. Mot. Pict. Eng.*, **11**, 607 (1927).

TABLE II

THE FLUORESCENCE OF HYDROLYZED GELATIN

Hours boiled....	0	0.33	0.55	1.33	2.25	5.00	24.00
Viscosity.....	17.8	14.5	11.5	7.6	5.1	2.4	1.55
Density.....	0.88	0.72	0.72	0.70	0.60	0.58	0.74

Sheppard and Houck[9] have concluded that diminution of the viscosity of gelatin sols by heating at elevated temperatures is to be accounted for by hydrolytic decomposition of the gelatin. The part of the hydrolysis reaction that causes the reduction of the viscosity, probably by the breakdown of large colloidal molecules, was complete in our experiment in the first five hours of heating and during this period the fluorescence of the sol in ultraviolet light showed a progressive decrease. In the interval between five and twenty-four hours, the solution became amber colored and the fluorescence makes a marked regain toward its initial value. No sensible change in viscosity took place during this time so it seems evident that the increased fluorescence must be associated with changes other than those of micellar nature that might be expected to alter the flow characteristics of the sol.

Discussion of Results

The results of this investigation are not in accord with the conclusions of previous experimenters that the fluorescence of cellulose derivatives is independent of the physical form of the material and related only to changes in chemical composition, and that the fluorescence of gelatin in ultraviolet light becomes more intense as the material is subjected to progressive disgregation. Enough data have been presented in the present paper to prove that: (a) the fluorescence excited by ultraviolet light in cellulose acetate and nitrate films depends on the micellar structure of the film; (b) when the micellar structure is similar, acetates resemble each other in fluorescence when they are alike in chemical composition rather than in colloidal properties; (c) the fluorescence of cellulose acetate sols is independent of the colloidal properties of the sol; (d) the fluorescence of gelatin sols decreases during the part of the hydrolysis causing a change in micellar magnitude and increases later because of some secondary change.

It seems likely that the amount of strain in a cellulose acetate or nitrate film affects the fluorescence of the film and that the effect is different for cellulose ester films made from different materials. The "temporary dichromatism" observed by Kundt[10] and quantitatively investigated by Pulfrich[11] in the case of stretched rubber affords an interesting suggestion as to the cause of the observed change in fluorescence in stretched cellulosic

[9] S. E. Sheppard and R. C. Houck, *J. Phys. Chem.*, **34**, 273 (1930).

[10] A. Kundt, *Ann. Physik*, Old Series, [1] **151**, 125 (1874).

[11] C. Pulfrich, *ibid.*, New Series, **14**, 193 (1881).

films. If the absorption coefficients for different wave lengths in the ultraviolet shift independently of each other as a cellulose acetate or nitrate film is stretched, as they do in the visible region in the case of rubber, the amount of fluorescent light emitted by these wave lengths would vary as the energy absorbed varied. It is planned to investigate this matter further.

The evidence seems conclusive that as far as the λ365 mμ is concerned, the fluorescence of gelatin in ultraviolet light decreases as the aggregates responsible for the high viscosity of the sol are broken up. The subsequent increase in fluorescence is connected with some other change in the solution. The darkened color of the solution suggests that humin formation accompanied by partial oxidation and carbonization had taken place. Brooks[12] has remarked that the formation of fluorescent material is almost universally observed when organic material is partially carbonized by heat, which indicates an explanation for our observed rise in the fluorescent power of the solution.

Summary

The intensity of fluorescence of cellulose nitrate and acetate films in ultraviolet light depends on the wave length of the exciting radiation, and the chemical composition and the micellar structure of the film. The intensity of fluorescence of acetone solutions of cellulose acetate in light of wave length 365 mμ is independent of the colloidal properties of the solution. A decrease in the viscosity of gelatin solutions caused by hydrolytic disgregation of micellar structures is accompanied by a decrease in the intensity of fluorescence in light of wave length 365 mμ. Subsequent chemical changes cause an increase in the fluorescence.

ROCHESTER, NEW YORK

[12] B. T. Brooks, "Non-Benzenoid Hydrocarbons," The Chemical Catalog Company, New York, 1922, p. 549.