furnace. The cylindrical cleavage plane was very distinct. There was a dark gray incrustation between the layers, and in many places bubbles had developed between the layers. The same phenomenon was observed in a second combustion tube which was used similarly for about the same length of time.

Summary

An improved apparatus for the preparation of ketene from acetone is described. The temperature, the rate of flow of acetone, and the percentage decomposition of acetone all influence the yield of ketene.

For practical purposes, the following conditions seem best for ketene production: temperature, 695–705°; rate of flow of acetone, 5 cc. per minute, and the decomposition of acetone, between 25 and 40% of that introduced. These conditions give consistent yields of ketene which range between 35 and 45%.

The glass combustion tube becomes stratified after it has served in a number of runs. No ketene results when the glass tube is replaced by an iron pipe. Carbonization occurs instead, at temperatures which would allow ketene production.

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[Contribution from the Research Laboratory of the Eastman Kodak Company, No. 226]

THE PLASTICITY OF CELLULOSE IN CUPRAMMONIUM HYDROXIDE[1]

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Received November 24, 1924 Published May 5, 1925

In recent years no little interest has been shown in the viscosity of solutions of cellulose in cuprammonium hydroxide. It has been shown by Ost[2] and others[3] that cotton which has been bleached or treated with sodium hydroxide or even hot water will give a solution in cuprammonium hydroxide which has a lower viscosity than will an untreated cotton.

Joyner put forward the hypothesis that the viscosity in Schweitzer's reagent was dependent on a hypothetical substance which he called "cellulose A." Inasmuch as he had proved that the logarithm of the viscosity of cotton in cuprammonium hydroxide was proportional to the total cotton concentration, he assumed that, in a given cotton, the logarithm of the viscosity would be proportional to the "cellulose A" content and that he

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[1] Read at the Ithaca Meeting of the American Chemical Society, September, 1924.

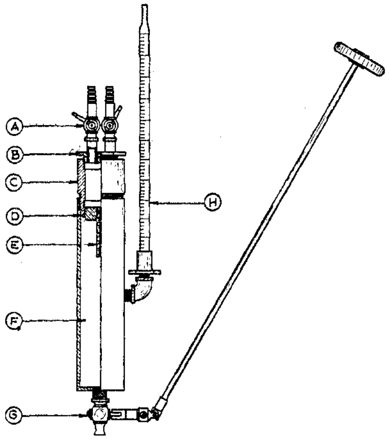
[2] Ost, *Z. angew. Chem.*, **24**, 1892 (1911).

[3] (a) Gibson, Spencer and McCall, *J. Chem. Soc.*, **117**, 479 (1920). (b) Joyner, *ibid.*, **121**, 1511, 2395 (1922). (c) Farrow and Neale, *J. Text. Inst.*, **15**, p. 157T (1924).

could, therefore, determine the "cellulose A" content by measuring the viscosity of the solution. He investigated the rate of the reaction between sodium hydroxide and cellulose by measuring the rate of fall of viscosity as the cotton was heated with the caustic soda.

Now cellulose in cuprammonium hydroxide is a plastic substance instead of a viscous liquid. In other words, the rate of flow of one liquid layer over the other is not proportional to the force applied. This means that ordinary viscosity determinations are likely to be meaningless and that Joyner's results might have been dependent on the particular sort of instrument used.

It appeared desirable, therefore, to determine the plasticity curves of cellulose of various concentrations in cuprammonium hydroxide and from these curves to determine whether the results obtained by Joyner would have been the same if he had used another type of viscometer, or another weight of steel ball in his falling-sphere viscometer.



Modified Bingham Plastometer.

Fig. 1.

A, Air-tight valves; *B*, Removable cap; *C*, Copper chamber; *D*, Removable copper plug; *E*, Capillary tube; *F*, Toluene chamber; *G*, Drain cock; *H*, Graduated tube.

The form of plastometer used by us (see Fig. 1) is a modification of that designed by Bingham and Green.[4] Instead of weighing the liquid that runs through the capillary tube, we measured the volume of toluene displaced by the liquid in the graduated tube H. This apparatus is far more rapid and appeared to us to be more accurate than that of the Bingham and Green design. Although a more recent apparatus of Bingham and Murray[5] is still more rapid, the added gain appeared to be hardly worth while for our purpose. Moreover, the criticisms of Green[6] make further work desirable before this instrument can be used with confidence.

The capillary tube used was 41.34 mm. long and 0.5016 mm. in diameter. The bore was measured at several places in the tube by means of a mercury thread and was constant within 0.5%. The ends of the bore were circular to within 1%.

Two methods were used for making the cuprammonium hydroxide. The first method consisted in running ammonia through a tower containing copper shavings in the presence of oxygen. The tower was cooled to 5° to 10° by means of ice or cold water. The procedure will be obvious from an inspection of Fig. 2. The ammonia was run through the tower six

[4] Bingham and Green, *Proc. Am. Soc. Test. Mat.*, **19**, ii, 640 (1909).

[5] Bingham and Murray, *ibid.*, **23**, ii, 653 (1923).

[6] Green, *ibid.*, **23**, ii, 663 (1923).

or eight times and analyzed for copper and ammonia. If the copper content was found to be high enough, the solution was diluted to the required concentration of copper and ammonia. The second method was to prepare copper hydroxide according to the method of Dawson[7] and dissolve it in ammonia. One kilogram of cupric sulfate pentahydrate was added to three liters of distilled water and the solution brought to the boiling point. While boiling, 28% ammonia water was added in small quantities during rapid stirring until a permanent cuprammonium blue just appeared. After washing the precipitate it was stirred mechanically for 15 hours in a 4% solution of sodium hydroxide, when the crystals became dark blue in color. It was then filtered and washed many times until the wash water gave no test for alkali or sulfate. After drying in a vacuum the precipitate showed 62% of copper instead of the theoretical 65%. In the present research, sufficient copper hydroxide was dissolved in aqueous ammonia to make a solution containing 1.5 g. of copper and 20.5 g. of ammonia to each 100 g. of solution.

The cellulose used was supplied by Mr. Gray and Mr. Corey of this Laboratory and was made according to their method for preparing standard cellulose.[8] All the results reported here were obtained with a single sample of the material.

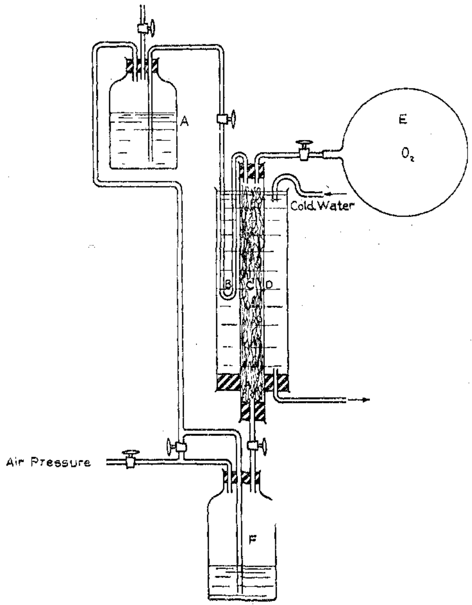


Fig. 2.—Apparatus for making cuprammonium hydroxide.

A, 3 gallon bottle; *B*, Cooling coil; *C*, Copper wool; *D*, Cooling bath; *E*, Rubber balloon; *F*, 3 gallon bottle.

Complete exclusion of air during the solution of the cotton and during the measurements appears to be the most necessary precaution. A few cubic centimeters of air will reduce the viscosity many per cent.

It was found that the addition of 1 or 2% of cuprous ammonium hydroxide to the Schweitzer's reagent helped to prevent oxidation. Cane sugar, also, as has been shown by other workers,[3b] tends to reduce the effect of air. In the results reported here, 2 g. of cane sugar was added to each 100 g. of the solution.

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[7] Dawson, *Z. physik. Chem.*, **69**, 110 (1909).

[8] Gray and Corey, *Ind. Eng. Chem.*, **16**, 853, 1130 (1924).

The solutions were made up as follows. Two g. of cellulose, 2 g. of cane sugar and 2.3 g. of cupric hydroxide were placed in a 150cc. brown glass bottle, fitted with a ground-glass stopper and provided with an inlet and outlet tube as in a wash bottle. The inlet tube was connected by a two-way stopcock to a source of hydrogen and a vacuum. The outlet tube was connected to a separating funnel containing the required amount of ammonia. After the bottle had been repeatedly rinsed with oxygen-free hydrogen, the ammonia was admitted. The bottles were rocked for several hours in a thermostat at 25° and then transferred to the plastometer in a manner similar to the above. The solutions still contained minute specks of undissolved material, the nature of which is uncertain.

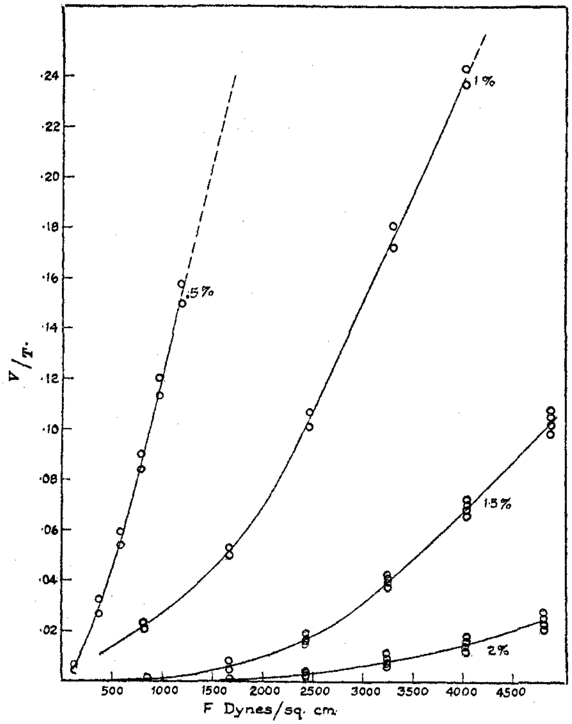

Fig. 3.—Plasticity curves, cellulose in cuprammonium hydroxide at various concentrations.

The pressure was applied to the plastometer by means of air in a tank, the pressure being measured by an open-tube mercury manometer about two meters high. As the volume of liquid flowing through the capillary was very small compared to the volume of the tank, the pressure was practically constant during a determination. A single plasticity curve could be determined in ten or fifteen minutes, during which time the effect of the air at the top of the chamber on the viscosity of the liquid at the bottom of the chamber was negligible.

The results are plotted in Fig. 3. They can be read with an accuracy equal to that of the data. The ordinates are cc. per second of liquid flowing through the capillary and the abscissas are dynes per sq. cm. at the capillary wall, as obtained by the formula of Bingham,[5] $F = Pr/2L$, where F is the force per sq. cm. at the capillary surface, P the pressure per sq. cm. in dynes, r the radius of the capillary tube and L the length of the capillary tube.

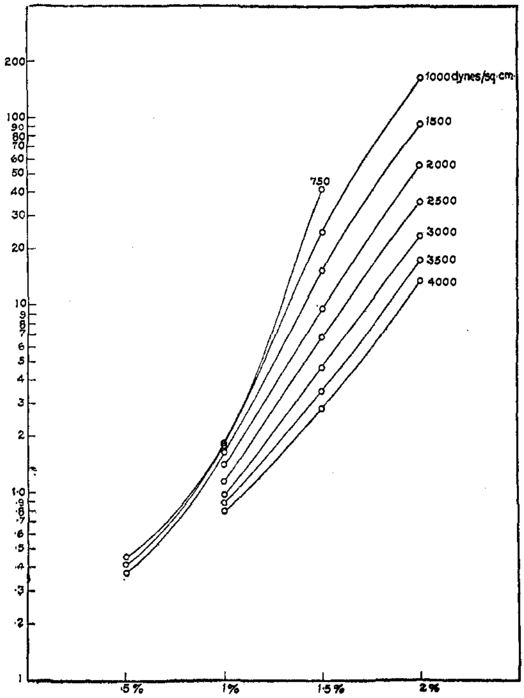

Fig. 4.—Apparent viscosity of cellulose in cuprammonium hydroxide as a function of the concentration at different shearing forces.

In order to determine whether or not the law observed by Joyner is a general one, the viscosity as obtained by Poiseuille's formula is plotted against concentration on semi-log paper (see Fig. 4). Each line represents a viscosity-concentration curve at a different shearing force. It will be observed that the lines are nearly straight except at the low pressures where the results are less accurate. This means that Joyner's law, that the log of the viscosity is proportional to the concentration of cellulose in Schweitzer's reagent, holds for the shearing forces we studied. Fig. 4 shows strikingly how the apparent viscosity varies as the shearing force is varied. The 2% solution, for example, appears to have a viscosity of 160 poises at a shearing force of 1000 dynes per sq. cm., and a viscosity of 13 poises at a shearing force of 4000 dynes per sq. cm.

Summary

1. The Bingham and Green plastometer has been improved.
2. Plasticity curves for cellulose in cuprammonium hydroxide have been obtained.
3. The results obtained by Joyner have been confirmed.

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