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THE ACTION OF FATTY ACIDS ON CELLULOSE[1]

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When cellulose is heated with acetic acid, no obvious change in the external appearance of the fibers takes place, but esterification occurs and the resulting product contains combined acetyl. While an analogous action has been observed with anhydrous formic acid,[2] none appears to have been recorded in the cases of its homologs. We have found esterification to take place on boiling cellulose not only with acetic acid, but with the higher members of the series up to heptylic. The rates of esterification in these cases are lower than with acetic acid, apparently decreasing with rise in molecular weight.

The esterification of native cellulose fibers in this way tends to a limit expressed by the formula $C_{24}H_{39}O_{20}(COR)$, which in the case of acetic acid and propionic acid is reached after about one hundred hours of boiling under atmospheric pressure. The same result is reached in a shorter time by heating to a higher temperature, either under pressure or in the superheated vapor of the acid. On continuing the action for a prolonged time after this point is reached, esterification ceases, or occurs to only a very slight extent and very slowly (an effect which we incline to attribute to incipient decomposition of the cellulose under the drastic conditions of temperature). This approximate limit is observed with all forms of native cellulose and appears to be independent of the state of aggregation (indicated by the cuprammonium viscosity of the starting material).

When, on the other hand, the native cellulose is replaced by hydrated cellulose, such as rayon prepared from viscose, from cuprammonium solutions or by denitration of nitrocellulose, esterification tends toward a limit expressed by the formula $C_6H_9O_5(COR)$. The same is observed for mercerized cellulose and for cellulose obtained by saponification of precipitated cellulose acetate.

From these observations it must be concluded that, firstly, in native cellulose one hydroxyl group out of every twelve is chemically different from the rest, being capable of esterification without the intervention of acid anhydrides or of catalysts. The fact that one hydroxyl group out of twelve displays distinctive chemical properties is, in our opinion, an argument for regarding native cellulose as a multiple of the unit $C_{24}H_{40}O_{20}$.

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[1] The results here described form the subjects of U. S. Patents 1,668,944 and 1,668,945 of 1928 and of pending applications.

[2] See E. C. Worden and L. Rutstein, *Kunststoffe*, 2, 325 (1912), for a summary of work on this subject.

Secondly, in hydrated cellulose four such hydroxyl groups are chemically different from the remaining eight.

The introduction of acyl groups to this limited extent causes no substantial alteration in the general appearance of the cellulose treated, beyond a tendency of the fibers to become weaker and more friable. Apart from the fact that they are hydrolyzed by alkali, the low esters are indistinguishable in chemical and physical properties from cellulose, being insoluble in organic liquids, but soluble in Schweitzer's reagent, in concentrated sulfuric or phosphoric acid, and in concentrated zinc chloride. The only marked difference which has been observed is concerned with the action of dyes, and is restricted to the more highly esterified products which are obtained from hydrated cellulose. Thus prolonged boiling with acetic acid confers upon rayon fibers the ability to retain basic dyes, such as Fuchsin and Malachite Green, which are quite inactive toward cellulose in its ordinary forms.

Investigation of saponified cellulose acetates indicates that fibers regenerated (by saponification) from cellulose which has been acetylated heterogeneously yield, on boiling with acetic acid, a series of esters, the limiting composition of which appears to be considerably lower in acetyl than that of those obtained from cellulose regenerated from acetates which have been produced in solution. This difference in chemical behavior is in harmony with the observation of Herzog[3] that the same two types of regenerated cellulose differ in their Roentgen spectra, which correspond, respectively, to that of native cellulose and that of hydrated cellulose. Owing, no doubt, to partial hydration of the cellulose during the heterogeneous acetylation, the fibers regenerated from the acetate so prepared take up higher proportions of acetyl than do the fibers of pure native cellulose, but the amounts are much lower than with cellulose regenerated from acetate which has been in solution.

Experimental

The general procedure adopted in the boiling experiments was as follows: the air-dried cellulose was immersed in 20 to 30 times its weight of glacial acetic acid in a round-bottomed pyrex flask; and gently boiled on an air-bath under reflux. The upper end of the condenser was fitted with a calcium chloride tube to prevent the access of atmospheric moisture. After a few hours of boiling, the heating was discontinued and as much of the acid as possible drained from the cellulose in order to remove soluble impurities as well as moisture originally present and formed by reaction. Fresh acid was added and boiling continued. Samples were periodically removed, thoroughly washed with distilled water and dried for analysis.

When operating with the higher acids, the reflux condenser was replaced by a fractionating column by means of which the water could be removed from the mixture. This system was also occasionally applied to the case of acetic acid.

For analysis, 1-g. samples were suspended in 20 cc. of 75% ethyl alcohol and warmed

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[3] R. O. Herzog, *Ber.*, **60**, 600 (1927).

for half an hour at 50–60°, then treated with 20.0 cc. of 0.5 *N* aqueous sodium hydroxide. After holding at 50–55° for fifteen minutes, the mixture was allowed to stand, well stoppered, for forty-eight hours at room temperature. The excess alkali was then titrated with 0.5 *N* acid, using phenolphthalein. It was found possible, in the case of the acetic esters, to reduce the time to twenty-four hours, but for the esters of higher acids the full forty-eight hours were found necessary.

The following experiments are typical of a very large number.

Surgical Cotton (High Viscosity) Boiled with Acetic Acid

Time, hours	0	1	2	4	8	16	24	48	72	96
Acetyl, %	0.6	0.8	1.3	2.4	2.9	3.7	4.5	5.5	6.0	6.2

The formula $C_{24}H_{39}O_{20}(COCH_3)$ requires CH_3CO = 6.2%.

Surgical Cotton Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	4.6	5.5	6.0	6.6	6.5	6.8	6.4

At the end of 500 hours, the cotton had become considerably disintegrated.

Linters (Medium Viscosity) Boiled with Acetic Acid

Time, hours	24	48	96	144	200	300
Acetyl, %	4.0	4.9	5.1	5.5	6.2	6.4

Linters (Low Viscosity) Boiled with Acetic Acid

Time, hours	24	48	96	200	300
Acetyl, %	4.4	5.0	5.6	6.9	6.8

Commercial Sulfite Pulp Boiled with Acetic Acid

Time, hours	24	48	96	200	300
Acetyl, %	5.1	5.6	6.7	7.6	7.5

This sample of sulfite pulp contained about 90% of α-cellulose and some colored impurities soluble in hot acetic acid.

Surgical Cotton Boiled with Propionic Acid

Time, hours	24	48	96	160	200
Propionyl, %	4.7	5.7	6.4	7.9	8.0

The cotton had become badly degraded after 200 hours. The formula $C_{24}H_{39}O_{20}(COC_2H_5)$ requires C_2H_5CO = 8.1%.

Linters (Medium Viscosity) Boiled with Propionic Acid

Time, hours	24	48	96	144	200
Propionyl, %	6.7	7.4	7.8	8.0	8.2

Linters (Medium Viscosity) Boiled with *n*-Butyric Acid

Time, hours	24	48	96	144	200
Butyryl, %	5.0	5.9	8.6	10.2	10.9

The formula $C_{24}H_{39}O_{20}(COC_3H_7)$ requires C_3H_7CO = 9.9%.

Surgical cotton was also heated with acetic acid in sealed glass tubes to 140–145°.

Time, hours	8	16	24	48
Acetyl, %	4.6	5.7	7.4	7.5

The last two samples were somewhat degraded.

Surgical cotton was heated to 150–155° in a current of acetic acid vapor.

Time, hours	6	7	20
Acetyl, %	3.8	4.0	6.0

In the following four experiments, commercial samples of artificial silk, prepared by different processes, were employed. They show very clearly that the acetyl content tends to a limit not far removed from the 21.1% required by the formula $C_6H_9O_5(COCH_3)$.

Viscose Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	10.2	11.6	14.5	20.0	21.2	22.2	22.3

Cuprammonium Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600	700
Acetyl, %	8.2	10.8	14.6	19.0	20.9	22.0	22.2	22.4	22.1

Denitrated Nitrocellulose Rayon Fibers Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500
Acetyl, %	9.1	11.0	13.2	18.5	20.6	21.6	22.0

The same effect is found with cellulose after mercerization. Surgical cotton was soaked for twenty-four hours at 20° in 18% and in 40% sodium hydroxide solution, well washed with water, finally with acetic acid and boiled with acetic acid.

Cellulose Mercerized with 18% NaOH Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600
Acetyl, %	9.3	11.6	13.5	17.5	19.2	20.9	21.6	21.9

Cellulose Mercerized with 40% NaOH Boiled with Acetic Acid

Time, hours	24	48	96	200	300	400	500	600
Acetyl, %	10.2	13.0	14.8	17.6	19.5	22.2	22.6	22.6

A sample of surgical cotton, mercerized with 18% sodium hydroxide for twenty-four hours at 20°, was heated to 150–155° in a current of acetic acid vapor.

Time, hours	6	12
Acetyl, %	6.7	9.5

Cellulose acetate was prepared by a standard method, using acetic anhydride and a mineral acid catalyst in acetic acid. The resulting solution was poured into water and the amorphous precipitate thoroughly washed. It contained 44.5% of acetyl. It was then completely saponified by the process (described above) for the determination of acetyl, well washed with water and finally with acetic acid, and boiled with acetic acid.

Time, hours	0	24	48	96	200	300	400	500
Acetyl, %	0.0	10.0	12.0	14.2	17.8	20.2	22.3	22.2

Surgical cotton was acetylated by a standard method employing acetic anhydride and a mineral catalyst in carbon tetrachloride. The resulting product, which preserved the original fibrous structure of the cotton, contained 43.6% of acetyl. It was completely saponified by the same method as above, well washed with water and finally with acetic acid, and boiled with acetic acid.

Time, hours	24	48	96	200
Acetyl, %	6.7	7.6	9.8	10.8

After 300 hours of boiling, the fibers had become completely disintegrated.

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Summary

1. Native cellulose is esterified on heating with acetic acid, the reaction coming to an end when the resulting product contains 6–7% of acetyl. This corresponds to the composition $C_{24}H_{39}O_{20}(COCH_3)$. An analogous effect is produced with propionic acid and butyric acid.
2. Hydrated cellulose, prepared by regeneration of cellulose from its nitrate, from viscose, from its solution in Schweitzer's reagent or from dissolved cellulose acetate, yields, on heating with acetic acid, esters having a limiting composition expressed by the formula $C_6H_9O_5(COCH_3)$.
3. Mercerized cellulose behaves in the same way as hydrated cellulose.
4. Cellulose regenerated from cellulose acetate which has preserved its original fibrous structure behaves, in this reaction, more like native cellulose than hydrated cellulose.
5. In view of the definite limit of esterifiability of native cellulose by acids alone, it is concluded that the constitution of cellulose must be expressed as a multiple of the unit $C_{24}H_{40}O_{20}$.

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