Heterogeneous Structure of Rayon. III. Peeling-off by Heterogeous Nitration

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In the preceding papers[1] the authors studied the conditions of peeling-off the rayons by heterogeneous acetylation and reported some results obtained by applying this method for several types of rayons. The results are very interesting but it requires too long acetylation up to some hundred to one thousand hours at 60°C. and the reaction is followed by remarkable degradation of cellulose, which will

(1) S. Okajima, S. Hayama and K. Kobayashi, This Bulletin, **25**, 271, 275 (1952).

be a disadvantage in some cases.

As is well known, the ordinary nitration of cellulose proceeds very smoothy with little degradation, but the reaction velocity is too large to be used for our present purposes. Furthermore the ordinary nitration is said not to be fiber-heterogeneous. But according to S. Watanabe,[2] the nitration in organic diluents proceeds with moderate speed and in the case of the natural fibers the reaction seems to be fibrillar-heterogeneous under appropriate conditions. Therefore this type of nitration is very interesting also for our study and some peeling-off examination was made by nitration.

In this report the conditions under which the nitration proceeds fiber-heterogeneously with moderate speed are described and the radial distributions of the orientation degrees in some rayons obtained by this method are compared to those obtained previously by heterogeneous acetylation.

Conditions of Fiber-heterogeneous Nitration

Using a HNO_3—$(CH_3CO)_2O$—CCl_4 system as the nitration bath, the conditions in which a fiber-heterogeneous nitration proceeded with moderate speed was determined. Pieces of an ordinary viscose rayon on the market were extracted with ether and hot water (60°C.) as described previously, and were used as the samples by drying in vacuum immediately before nitration. After nitration for various hours at room temperature the samples were washed with CCl_4 and then thoroughly with water (60°C.) and air dried.

The reaction type varies with the composition of the acid mixture, which was examined by observing the nitrated products under a polarization microscope. If the reaction is fiber-heterogeneous the nitrated sheath of each filament can be clearly recognized, as the birefringence of the cellulose differs remarkably from that of the nitrocellulose.[3] And moreover when such a fiber is swollen in the acetone-water mixture (2:1) only the nitrated sheath swells and a clear demarcation appears between the nitrated and unreacted parts of celluloses and after dissolving away with pure acetone, a slender core remains, which shows some lateral striations as does the original fiber. A permutoid reaction does not indicate such a behavior and the fiber swells homogeneously. Therefore the reaction type can easily be distinguished by such tests.

As to the conditions, dilution ratio DR, nitric acid ratio NAR and bath raio BR are defined as follows:

DR: Weight of $HNO_3+(CH_3CO)_2O$/Weight of CCl_4,

NAR: Weight of HNO_3/(Weight of $HNO_3+(CH_3CO)_2O$),

BR: Weight of the total acid mixture/Weight of the cellulose.

The reaction velocity is dependent on these factors, and the conditions are selected in such a way that the nitration is completed in about 7 hours at room temperature.

The results are summarized in Tables 1 and 2, according to which the following facts are seen: (1) DR has little effect on the type of reaction and the velocity within such experiments. (2) NAR are very effective and at 55% NAR the reaction is too speedy to be followed and at 45% it is too slow. (3) NAR affects also the type of reaction; at 55% NAR the fiber extracted with acetone becomes slender but the lateral striations disappear, and the nitration is of slight permutoid.

Table 1

Effect of the Bath Composition, $T=20$°C.

Exp. No.	DR	NAR(%)	t (hr.)	Reaction type
1	1/5	50	2	F. H.*
2	1/10	50	2	F. H.
3	1/10	50	15	Completely reacted
4	1/5	55	0.5	F. H.
5	1/5	55	1	Completely reacted
6	1/5	45	22	F. H. but the reaction is too slow

* Fiber-heterogenous

Table 2 indicates the effect of AR, according to which the yarn reacts too rapidly at AR=1/2.5 and the optimum value is 1/5~1/10.

Table 2

Effect of DR and BR, T=13°C. and NAR=50%.

Exp. No.	DR	BR	t (hr.)	Type of reaction
1	1/2.5	230	3	Completely reacted
2	1/5	200	3	F. H.
3	1/10	182	3	F. H.
4	1/15	178	3	F. H.
5	1/20	175	3	F. H.
6	1/10	182	8	Nearly completely reacted

To summarize, the best conditions for our purpose are as follows:

DR=1/5~1/20,

NR=50%,

providing $t=0$~7 hrs and T=15~20°C.

Peeling-off by Nitration

The conditions of nitration used for peeling-off is now determined; it is applied to some rayon samples. Those results are summarized in the following tables and figures, where the notations used are the same as described previously unless being noted specially.

(2) S. Watanabe, *J. Soc. Chem. Ind. Japan*, **45**, 832 (1942), **47**, 561 (1944).

(3) Ambronn und Frey, "Polarisationsmikroskop", 1926, S. 169; K. Kanamaru, *Helv. Chim. Acta*, **18**, 1429 (1934).

Table 3

Viscose Rayon V−1

(1) NAR=50%, DR=1/10, BR=180, T=18°C.

Not denitrated. * indicates the value after denitration.

t, hr	5/61	10/60	25/60	1	2	3-20/60	4-40/60	7
$W'/W-1$, %	4.1	6.0	9.2	14.2	21.8	26.0	41.1	55.0
L_T/W, %	3.1	5.1	8.7	14.2	21.4	30.7	44.5	55.7
N, %	1.01	1.74	2.54	3.68	5.28	6.11	8.40	10.05
$x/3(N)$, %	4.0	7.0	10.6	16.0	24.2	29.3	44.3	57.2
$x/3$, %	4.9	7.2	11.0	17.0	26.2	31.2	49.3	66.0
P_r, %	1.6	2.6	4.4	7.4	11.4	16.8	25.5	33.4
$\Gamma \cdot 10^3$	21.5	—	18.2	17.5	16.0	16.2	—	—
$\Gamma \cdot 10^3$*	20.4	21.2	19.6	17.0	17.1	16.2	16.5	16.3

(2) NAR=50%, DR=1/10, BR=150, T=18°C.

Not denitrated.

t, hr	5/60	10/60	25/60	1	2	3-30/60	5-15/60	7-20/60
$W'/W-1$, %	4.4	5.7	8.2	13.2	19.3	28.4	36.2	53.5
L_T/W, %	6.5	5.4	7.5	8.2	—	26.8	34.3	—
N, %	1.27	1.49	2.38	3.42	4.50	6.60	7.70	9.25
$x/3(N)$, %	5.0	5.9	9.9	14.8	20.0	32.7	40.1	51.3
$x/3$, %	5.3	6.8	9.8	15.8	23.2	34.1	42.2	64.2
P_r, %	2.6	2.7	3.8	4.3	—	14.4	19.0	—
$\Gamma \cdot 10^3$	—	—	—	—	—	—	—	—

Table 4

Cuprammonium Rayon C

(1) NAR=50%, DR=1/10, BR=220, T=18.5°C.

Not denitrated. * indicates the values after denitration.

t, hr	5/60	10/60	25/60	
$W'/W-1$, %	24.9	39.2	69.0	
L_T/W, %	20.2	36.6	72.5;	77.2*
N, %	5.78	8.94	12.34	
$x/3(N)$, %	27.3	49.0	79.5	
$x/3$, %	29.9	47.0	82.8	
P_r, %	10.8	20.4	47.5;	52.2*
$\Gamma \cdot 10^3$	—	—	—	28.1*

(2) NAR=50%, DR=1/15, BR=212, T=16°C.

Not denitrated.

t, hr	5/60	9/60	15/60	26/60	42/60
$W'/W-1$, %	6.3	13.8	19.3	29.0	38.3
L_T/W, %	3.4	4.8	12.8	25.8	36.0
N, %	2.17	3.39	4.64	7.15	8.70
$x/3(N)$, %	8.9	14.6	20.8	36.2	47.2
$x/3$, %	7.6	16.6	23.2	34.8	46.0
P_r, %	1.7	2.4	6.5	13.6	20.0
$\Gamma \cdot 10^3$	—	—	—	—	—

(3) NAR=46%, DR=1/10, BR=154, T=14°C.

Denitrated. "L_T/W* indicates the values before denitration.

t, hr	3/60	6/60	12/60	24/60	50/60	30/60**	35/60***
$W'/W-1$, %	3.1	6.1	9.2	15.4	21.8	39.0	42.8
L_T/W*, %	0.0	0.0	1.9	10.3	19.3	35.6	37.3
L_T/W, %	2.6	4.8	—	15.4	23.8	40.6	42.0
N, %	1.06	1.95	2.52	3.75	5.55	7.97	9.25
$x/3(N)$, %	3.3	8.0	10.3	16.7	26.1	42.1	51.1
$x/3$, %	3.7	7.3	11.0	18.5	26.2	46.8	51.4
P_r, %	1.3	2.4	—	8.0	12.7	22.9	23.8
$\Gamma \cdot 10^3$	31.4	31.8	—	31.3	30.8	30.4	29.9

** NAR=56%, DR=1/10, BR=220, T=2°C.

*** NAR=60%, DR=1/10, BR=220, T=2°C.

Table 5

Tire cord T

(1) NAR=50%, DR=1/10, BR=220, T=12°C. Denitrated. L_T/W^* indicates the values before denitration.

t, hr	40/60	1	1-20/60	1-40/60	2
$W'/W-1$, %	16.2	22.8	29.0	38.3	46.0
L_T/W^*, %	14.2	21.7	28.1	35.8	42.5
L_T/W, %	17.2	—	—	38.8	45.5
N, %	4.11	5.73	6.64	8.56	9.30
$x/3(N)$, %	18.1	27.1	33.0	46.2	51.3
$x/3$, %	19.4	27.4	34.8	46.0	55.2
P_r, %	9.0	11.1	15.5	21.6	26.2
$\Gamma \cdot 10^3$	33.6	—	—	32.7	32.0

(2) NAR=50%, DR=1/10, BR=220, T=10°C. Denitrated. L_T/W^* indicates the values before denitration.

t, hr	10/60	30/60	1-40/60	3-30/60
$W'/W-1$, %	5.6	10.2	20.1	53.1
L_T/W^*, %	3.1	7.9	19.4	53.0
L_T/W, %	5.5	10.1	—	56.1
N, %	1.54	2.66	4.81	9.26
$x/3(N)$, %	6.1	11.2	21.9	51.3
$x/3$, %	6.7	12.2	24.1	63.7
P_r, %	2.8	5.1	—	33.7
$\Gamma \cdot 10^3$	33.7	33.7	—	30.6

(3) NAR=50%, DR=1/10, BR=220, T=14°C. Denitrated. L_T/W^* indicates the values before denitration.

t, hr	55/60	1-50/60	2-20/60	3
$W'/W-1$, %	26.6	56.9	71.1	85.2
L_T/W^*, %	24.8	55.8	73.4	—
L_T/W, %	27.7	—	76.0	—
N, %	5.91	9.92	11.28	—
$x/3(N)$, %	28.1	56.1	67.9	—
$x/3$, %	31.9	68.3	85.3	—
P_r, %	15.0	33.5	51.0	—
$\Gamma \cdot 10^3$	33.2	—	30.4	—

Some of the previous samples are used also here in order to compare the acetylation and nitration results.

The notation in the above tables are defined below:

t: Duration of nitration, hr.
W: Weight of the sample used for nitration, g.
W': Weight of the nitrated yarn, g.
L_T/W: Extracted portion (by acetone) of the nitrated yarn. The percentage is expressed on the cellulose base.
N: Nitrogen content (%) of the nitrated yarn, determined with Lunge nitrometer.
P_r: Peeled-off portion of the single filament, expressed on the percentage of the original diameter.

Experimental Results

(1) **Nitration.**—In Fig. 1 the weight increase W'/W is plotted against the nitrogen content of the nitrated yarn, where the curve is the theoretical relation. The observed points of cuprammonium yarn (×) are on the theoretical curve, but the highly nitrated products of the other two samples (○ and ▲) deviate upward from the relation. The cause is not yet clear but this is certainly because the nitrogen content which is obtained is too low; of course in the case of the cuprammonium yarn it is said to be correctly obtained. Then it can be said, at least, that no part of the nitrated yarn disperses away in the nitration bath as the yarn does during acetylation, and then $\log(W'/W-1)$ versus $\log t$ is expected to be linear. Fig. 2 shows that this is the case.

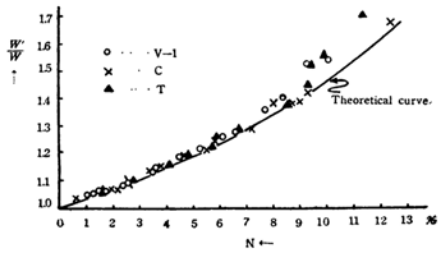


Fig. 1.

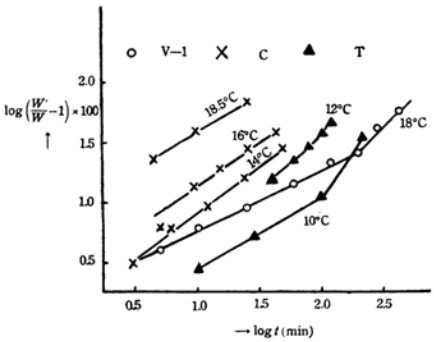


Fig. 2.

The knick points are seen on the relations of $V-1$ and T, but none on that of C. This relates probably to the existence of the skin, which will be studied precisely in the future.

The temperature coefficient of the nitration reaction is considerable.

(2) **The weight of the peeled-off portion.**—If the nitrated OH is x mols per 162 g of cellulose, W'/W is expressed by the following function of x.

$$W'W-1=45/162 \cdot x$$

Assuming now that all the NO_2-groups are concentrated to the nitrated shell to constitute

trinitrocellulose[1] and this triester is extracted by acetone to give L_T, then L_T/W must be $x/3$. These relations are shown in Fig. 3, where $W'/W-1$ is plotted on the abscissa instead of $x/3$. x can be also calculated from the observed values of N %, which is given in Table 3~5 by $x/3(N)$, but this value which is obtained seems to be too low and the discussion is now ommitted here.

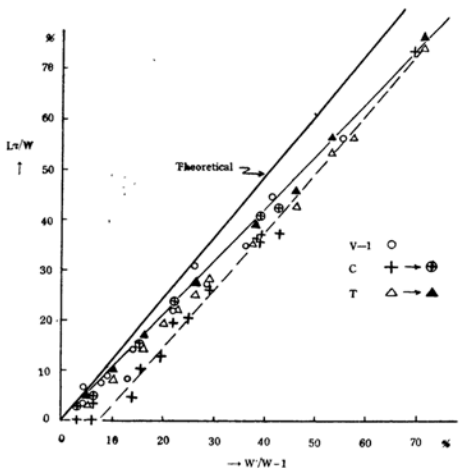


Fig. 3.

The observed points of each sample are on the separate lines, but they are all smaller than the corresponding theoretical values. It is worth while especially to note that the cuprammonium rayon whose N % is lower than 1.5% can not be extracted to any extent. This fact indicates that the assumption taken for the above calculation does not hold exactly and the next consideration can be given for one of the reasons.

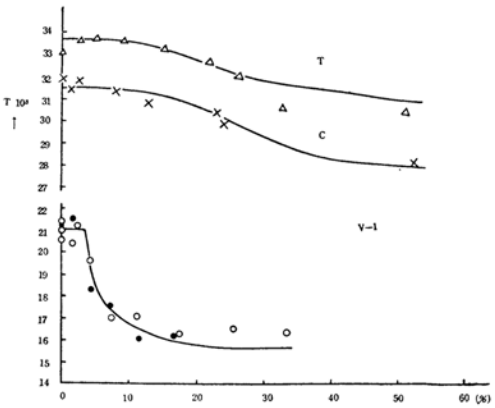
A diffuse layer may exist between the trinitrocellulose (in the practical meaning) shell and the cellulose core, part of which then remains unextracted on the cellulose core and gives a greater value of the unextracted residue W', if the residue is considered as described above, and therefore the extracted portion L_T will be smaller as compared to the value from $W'/W-1$. And indeed when the unextracted residue is treated with NH_4SH alcoholic solution, L_T/W approaches to the theoretical; In the figure the point △ of T and + of C shift to the corresponding values is indicated by ▲ and ⊕ respectively.

These corrected points belong to a line which starts from the origin, but the inclination of the line differs from that of the theoretical line. This means that the part of the diffuse layer remains undissolved and the amounts increase as the nitration proceeds because the layer as it diffuses, becomes broader and broader toward the center of the filament.

Of course acetone dissolves not only trinitrocellulose but also lower nitrates, so the above consideration is a first approximation. But in this case L_T/W calculated from W'/W must be still larger.

Radial Distribution of Γ

The thickness of the peeled-off shell, P_r, was calculated from the values of L_T/W, where the extracted yarn with acetone was followed by the complete denitration with NH_4SH alcoholic solution, which was prepared by the well known method.[1]



→ P_r

Fig. 4.

The intrinsic double refraction, Γ, of the peeled-off core was measured as described in the preceding paper. The double refraction of the extracted filament changes but slightly by denitration (rf. Fig. 4, ○ and ● of V—1 are the values before and after the denitration respectively) but the treatment is necessary to obtain the reasonable value of P_r, as the surface layer of the core contains some low substituted nitrocellulose before denitration.

The relation of Γ and P_r are shown in Fig. 4, where P_r of V—1 is exceptionaly calculated from L_T/W before denitration. Even in this case Γ is the double refraction after denitration. The observed points are plotted in the figure, where the curves are the relation taken from the second report of this series, obtained by the acetylation method. In the cases of the tire cord and cuprammonium rayons Γ of the original filaments differs tolerably from the corresponding values of the previous measurements, so the previous curves are shifted upwards in the figure so that the origins coincide in both measurements. This discrepancy of Γ is probably caused by the fact that the composition of the immersion liquids used for the present measurement of the refractive indices differs from those of the previous one. In the case of V—1 the same liquid compositions

(4) J. Chédin, *Kolloid. Z.* **125**, 65 (1952).

(5) Dorée, "The Method of Cellulose Chemistry", 1933, P. 227.

were used and such a phenomenon is not observed and therefore the correction is unnecessary.

Then the observed points nearly agree with the previous curves in all cases. So now it is proved that the nitration method is also suitable for the peeling-off and it is superior in some cases, where the speedy reaction with no degradation is required. Such examples will be reported in the near future.

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