

## Uniformity of Substitution During the Emulsion Xanthation of Cellulose\*

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Commercial cellulose xanthate has an average of one xanthate group per two glucose units. This does not infer, however, that the xanthate groups are uniformly distributed upon all of the cellulose chains. The heterogeneous nature of the reaction system would suggest that this is not the case. If the reaction is principally molecular in nature, the distribution of the xanthate groups would be expected to be quite uniform with respect to chain length. On the other hand, if the reaction is micellar, the distribution would be expected to be somewhat less than uniform. A summary of evidence supporting both of these reaction mechanisms for the formation of cellulose xanthate is available in the literature.<sup>1</sup>

Various fractionation methods have afforded a means for approaching this problem. Direct fractionation of viscose<sup>2</sup> and fractionation of the stable diethylacetamide derivative<sup>3-5</sup> have indicated that the shorter cellulose chains consume larger quantities of carbon disulfide than the longer chains. Such evidence would support a micellar heterogeneous reaction mechanism. Recent data<sup>6</sup> published while this work was in progress have indicated that the longer chains are more highly substituted, suggesting possibly another predominating mechanism.

This investigation is concerned with the uniformity in substitution for viscose prepared by the emulsion xanthation technique and two factors believed to influence the uniformity—namely, the degree of xanthation and the time of xanthation.

### CHARACTERIZATION OF THE COTTON LINTERS

Viscose-grade cotton linters (Type LMV, Buckeye Cellulose Corporation) were used throughout the experimental program. A portion of the linters

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was nitrated according to the procedure of Bennett and Timell.<sup>7</sup> The nitrate was fractionated from an acetone solution by the evaporation method of Timell.<sup>8</sup> The intrinsic viscosities were determined in ethyl acetate at  $20 \pm 0.002^\circ\text{C}$ . and were converted to the theoretical value for the trinitrate,  $[\eta]_T$ , by use of the Lindsley and Frank relationship.<sup>9</sup> The weight-average degree of polymerization,  $\overline{DP}_w$ , was calculated from the relationship derived by Flory et al.<sup>10</sup> The fractionation data for the cotton linters are summarized in Table I

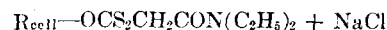
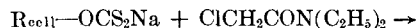
TABLE I  
Fractionation Data for Nitrated Cotton Linters

Fraction	Cumulative weight, %	$[\eta]_T$ , dl./g.	$\overline{DP}_w$
I	100.0	20.0	1930
II	85.7	16.4	1585
III	60.5	12.5	1210
IV	44.8	11.5	1115
V	41.1	10.9	1050
VI	37.0	8.87	862
VII	35.0	7.54	734
VIII	26.5	5.75	561
IX	21.1	4.31	422
X	5.5	3.59	352

### EXPERIMENTAL

Viscose was prepared by the emulsion xanthation technique described by Jayme et al.<sup>11,12</sup> at a temperature of  $20 \pm 0.02^\circ\text{C}$ . The total viscose prepared per sample bottle was approximately 350 g., depending upon the amount of carbon disulfide added. The corresponding cellulose concentration was about 2.4%; the sodium hydroxide concentration, about 13%.

The stable diethylacetamide derivative (DAX) was prepared in the usual manner<sup>3-6,13</sup> by reaction of the xanthate with *N,N*-diethylchloroacetamide, according to the following reaction:



A 1% solution of the derivative was prepared in 70% 2-chloroethanol. Precipitation was effected by successive additions of distilled water at 25°C. Each fraction was redissolved by raising the temperature to 35°C, followed by slow cooling to 25°C. The fractions were separated from the supernatant solution by centrifuging for 1 hr. at 1500 rpm. Each fraction was redissolved in 2-chloroethanol, reprecipitated by the addition of a large excess of water, and washed successively with distilled water, methanol, methanol-ether (1:1), and anhydrous ether.

The degree of substitution (DS) of the individual fractions was determined by the micro-Kjeldahl technique described by Timell and Purves.<sup>14</sup>

Reduced viscosities of the DAX fractions in 90% dimethyl sulfoxide (90 DMSO) were measured at  $25 \pm 0.02^\circ\text{C}$ . in an Ubbelohde dilution viscometer. The intrinsic viscosities were determined by extrapolation to zero concentration, according to the well-known Martin equation:

$$\log(\eta_{sp}/c) = \log[\eta] + k[\eta]c$$

Kinetic energy and shear corrections were negligible for the samples considered in this investigation.

The  $\overline{DP}_w$  of each fraction was calculated from the intrinsic viscosity in 90 DMSO according to the following relationship derived from light-scattering measurements:<sup>15</sup>

$$[\eta] = (5.63 - 3.35\text{DS}) \times 10^{-3}\overline{DP}_w$$

## EXPERIMENTAL RESULTS

### DAX Samples

The DAX derivatives prepared from the viscose are listed in Table II.

TABLE II  
DAX Samples

Sample	Xanthation time, hr.	CS <sub>2</sub> :cellulose ratio	Viscose, DAX, DS <sup>a</sup>	
			DS <sup>a</sup>	DS <sup>b</sup>
DAX A	6	1.04	—	0.59
DAX B	6	2.52	0.74	—
DAX C	6	2.96	1.11	1.02
DAX D	6	2.95	1.23	1.16
DAX E-1	1	1.48	—	0.27
DAX E-2	2	1.48	—	0.72
DAX E-3	3	1.48	—	0.79
DAX E-4	4	1.48	—	0.85
DAX E-6	6	1.48	—	0.95

<sup>a</sup> Determined by the ion-exchange method of Samuelson and Gärtner.<sup>16</sup>

<sup>b</sup> Calculated from the nitrogen content of the DAX derivative.

### Effect of Degree of Substitution on Fractionation

Equal amounts of DAX A (DS = 0.59) and DAX B (DS = 0.74) were mixed together to give a sample of average DS equal to 0.66. Subsequent fractionation of this mixed derivative led to the results summarized in Table III.

TABLE III  
Fractionation Data for DAX A-DAX B (DS = 0.66)

Fraction	Cumulative weight, %	DS	$[\eta]_{90\text{ DMSO}}$ , dl./g.
I	100.0	0.77	2.72
II	93.8	0.80	2.44
III	71.7	0.70	1.96
IV	50.0	0.66	3.65
V	32.2	0.54	2.98
VI	6.3	0.40	1.79
Weighted average (Fractions I-III)		0.75	2.27
Weighted average (Fractions IV-VI)		0.56	3.07
Weighted average (Fractions I-VI)		0.66	2.67

The weighted average DS from the fractionation was 0.66, indicating a negligible loss of acetamide groups. The viscosity values are somewhat surprising, in that the values for Fractions IV and V were significantly higher than that for Fraction I. It appears, however, that DAX A and DAX B have been successfully separated by this fractionation technique. This is borne out by the fact that Fractions I-III and Fractions IV-VI each comprise exactly 50% of the recovered derivative, and the average DS of each of these fraction groups corresponds well with the DS of the unfractionated derivatives. Evidently, where large differences in DS are involved, the fractionation is largely controlled by the degree of substitution. These results suggest that further work involving the fractionation of mixed derivatives might prove worthwhile in evaluating the factors influencing the course of fractionation.

### Effect of Substitution Level on the Uniformity of Substitution

DAX A (DS = 0.59), DAX C (DS = 1.02), and DAX D (DS = 1.16) prepared by 6 hr. xanthation were fractionated from aqueous 2-chloroethanol. In each case the weighted average DS determined from the fractionation data corresponded quite well with the DS of the unfractionated derivative. The fractionation yields were

TABLE IV  
Fractionation Data for DAX A (DS = 0.59)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	0.58	6.26	1700
II	89.0	0.57	5.39	1450
III	74.4	0.56	4.75	1260
IV	61.8	0.60	4.40	1210
V	52.3	0.57	3.93	1050
VI	47.0	0.54	3.64	948
VII	40.8	0.51	3.45	881
VIII	32.1	0.51	2.91	741
IX	26.9	0.49	2.50	628
X	23.2	0.49	2.38	596
XI	16.7	0.48	1.96	488
XII	10.0	0.56	1.58	420
XIII	4.1	0.56	1.18	314
Weighted average		0.55	4.00	1036

TABLE V  
Fractionation Data for DAX C (DS = 1.02)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	0.99	3.17	1370
II	92.7	1.00	3.21	1405
III	87.7	1.00	3.11	1365
IV	66.3	1.01	3.18	1415
V	61.6	0.95	2.91	1170
VI	45.5	0.92	2.67	1055
VII	33.7	0.96	2.29	947
VIII	22.5	1.00	1.89	830
IX	17.0	0.95	1.53	624
X	10.5	0.95	1.09	445
Weighted average		0.97	2.56	1083

TABLE VI  
Fractionation Data for DAX D (DS = 1.16)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	1.06	3.64	1925
II	98.2	1.19	3.52	2130
III	91.8	1.22	3.06	1960
IV	49.4	1.20	2.64	1630
V	43.6	1.22	2.30	1470
VI	38.2	1.17	1.90	1105
VII	31.4	1.21	1.68	1055
VIII	25.9	1.23	1.65	1085
IX	21.9	1.22	1.53	982
X	19.6	1.23	1.35	895
XI	16.8	1.18	1.28	758
XII	11.6	1.22	0.91	583
XIII	10.1	1.13	0.83	448
XIV	6.4	1.18	0.78	461
XV	4.2	1.08	0.59	292
XVI	2.1	1.18	0.38	222
Weighted average		1.21	2.38	1484

99, 87, and 91%, respectively. The fractionation data are summarized in Tables IV-VI.

### Effect of Xanthation Time on the Uniformity of Substitution

It would have been desirable to obtain fractionation data for DAX E-1 and DAX E-2; however, this was not possible due to the limited solubility of these derivatives in 2-chloroethanol. DAX E-3 (DS = 0.79), DAX E-4 (DS = 0.85) and DAX E-6 (DS = 0.95) were fractionated from aqueous 2-chloroethanol. The CS<sub>2</sub>:cellulose ratio was 1.48. The average DS obtained from the fractionation data corresponded well with the DS of the unfractionated derivatives. The yields were 93, 93, and 84%, respectively.

### DISCUSSION

The results reported for the fractionation of the mixed derivative DAX A-B are extremely interesting. Apparently, the derivatives have been separated with only a small amount of overlap in the fractions. Considerably more data are required before this phenomenon may be completely interpreted.

The weighted average  $\overline{DP}_w$  values obtained from the fractionation data (Tables IV-IX) were as follows: DAX A, 1035; DAX C, 1083; DAX D, 1484; DAX E-3, 882; DAX E-4, 1118; and DAX E-6, 1065. With the exception of DAX D and DAX E-3, these values corresponded well with the value for the original linters (1135). These results are in agreement with the conclusion of Jayme et al.<sup>11,12</sup> that degradation during emulsion xanthation is negligible.

The plots of DP versus DS for DAX, A, C, and D are shown in Figure 1. Similar plots for DAX E-3, E-4, and E-6 are shown in Figure 2. The

TABLE VII  
Fractionation Data for DAX E-3 (DS = 0.79)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	0.82	3.52	1219
II	76.5	0.82	3.43	1188
III	61.2	0.73	2.62	862
IV	46.5	0.80	2.58	870
V	36.3	0.79	2.18	730
VI	17.4	0.70	1.29	393
VII	9.5	0.68	1.00	298
Weighted average		0.78	2.61	882

TABLE VIII  
Fractionation Data for DAX E-4 (DS = 0.85)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	0.87	4.83	1775
II	75.3	0.84	3.42	1210
III	40.3	0.84	2.51	887
IV	25.4	0.80	1.78	600
V	9.2	0.81	0.78	268
Weighted average		0.84	3.12	1118

TABLE IX  
Fractionation Data for DAX E-6 (DS = 0.95)

Fraction	Cumulative weight, %	DS	$[\eta]_{90}^{\text{DMSO}}$ , dl./g.	$\overline{DP}_w$
I	100.0	0.97	4.66	1950
II	91.0	0.95	3.13	1280
III	41.5	0.94	2.44	980
IV	34.5	0.89	1.65	618
V	21.7	0.95	1.29	529
VI	12.0	0.87	1.29	475
VII	5.0	0.91	0.71	274
Weighted average		0.94	2.60	1065

TABLE X

Sample	Least-squares regression
DAX A	$DS = (5.71 \times 10^{-5}) \overline{DP}_w + 0.488$
DAX C	$DS = (4.51 \times 10^{-5}) \overline{DP}_w + 0.924$
DAX D	$DS = (3.37 \times 10^{-5}) \overline{DP}_w + 1.163$
DAX E-3	$DS = (14.50 \times 10^{-5}) \overline{DP}_w + 0.647$
DAX E-4	$DS = (4.38 \times 10^{-5}) \overline{DP}_w + 0.790$
DAX E-6	$DS = (4.57 \times 10^{-5}) \overline{DP}_w + 0.887$

calculated least-squares regressions are given in Table X.

Although the slopes are small, they appear to be consistent. Four of the six regressions fall within the 5% level of significance, while two (i.e., those for DAX C and DAX E-6) are slightly outside of the 5% level as determined by the *F*-test.

For given xanthation conditions, the general equation relating DS and DP may be written in the form:

$$DS = \beta \overline{DP}_w + DS_0$$

where  $\beta$  and  $DS_0$  are constants. For each of the fractionations the value of  $\beta$  was positive, indicating that the longer cellulose chains have a higher DS than the shorter chains. Indications are that an increase in the substitution level on increasing the amount of carbon disulfide in the system results in a more uniform distribution of the xanthate groups. Increasing the xanthation time also results in a more uniform distribution. Maximum nonuniformity (i.e., large values of  $\beta$ ) would be anticipated where the excess of carbon disulfide is small and the xanthation time is short.

Emulsion xanthation differs greatly from normal commercial viscose preparation, since in the case of emulsion xanthation the cellulose is suspended in an alkaline medium in the presence of a large excess of carbon disulfide. Concomitant xanthate formation and decomposition of the xanthate occur. The reactions involved may be represented as follows:

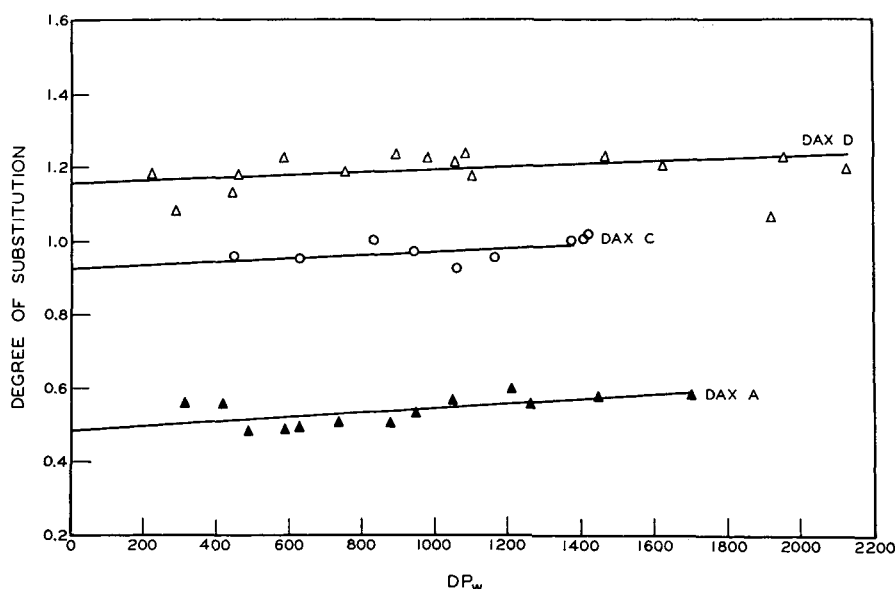


Fig. 1. Plot of DS vs.  $\overline{DP}_w$  for DAX A, C, D.

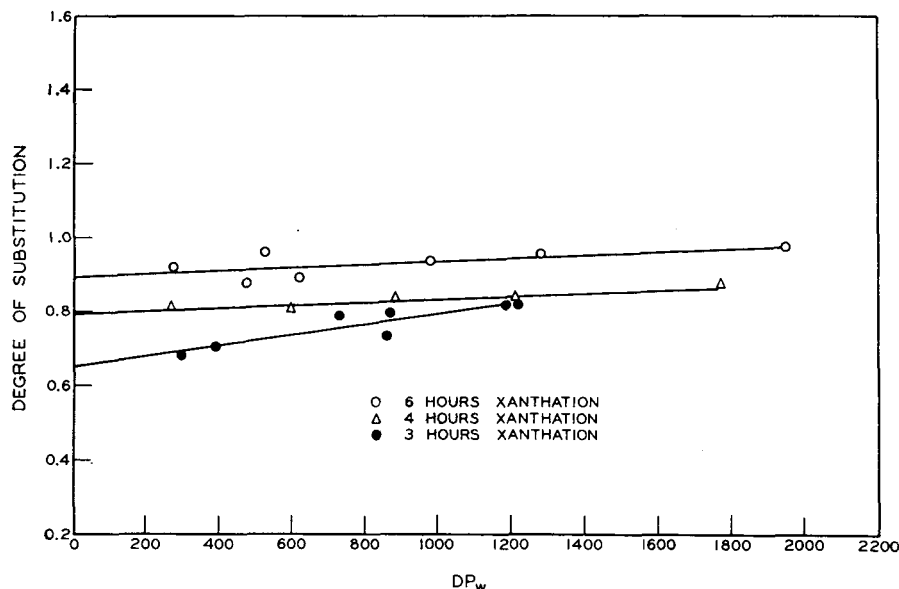


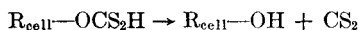
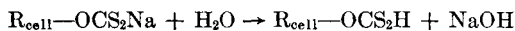
Fig. 2. Plot of DS vs.  $\overline{DP}_w$  for DAX E-3, E-4, and E-6.

Xanthate formation:

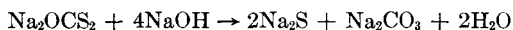
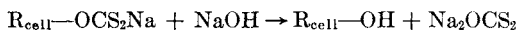


Xanthate decomposition:

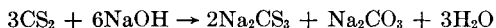
Hydrolysis:



Saponification:



In addition, carbon disulfide readily reacts with free sodium hydroxide as follows:



Indications from the fractionation data are that the longer cellulose chains are more highly xanthated than the shorter chains. This result was originally quite unexpected, since many of the reactions involved in the preparation of cellulose derivatives are micellar heterogeneous. (Since the time this work was originally started, however, Yamada and Mukoyama<sup>6</sup> have published results of a similar nature.) It appears that in the emulsion system factors other than the accessibility of the cellulose chains influence the mechanism of the xanthation reaction. On the basis of fractionation results, it is suggested that the following factors significantly control the mechanism of xanthation in the emulsion system.

1. During the initial stages of the reaction, the carbon disulfide is quite conceivably more concen-

trated at the surface of the cellulose fiber than in the bulk of the system. Xanthation occurs rapidly in the accessible regions of the cellulose fiber and at the micelle surfaces. Progressive dissolution of the cellulose xanthate occurs up to the point where all of the cellulose is in solution as the xanthate. The rate of xanthation of the undissolved cellulose xanthate is considerably higher than that for the dissolved xanthate due to the differences in carbon disulfide concentration.

2. Decomposition of the xanthate by hydrolysis and/or saponification occurs at a considerably higher rate for the dissolved xanthate than for the undissolved xanthate.

3. The net xanthation rate [actual xanthation rate (1) minus decomposition rate (2)] is higher for the undissolved xanthate than the dissolved xanthate.

The net result of these considerations is a maximum nonuniformity in substitution with regard to chain length during the early stages of the xanthation reaction. Following complete solution of the xanthate at a DS of slightly less than 0.5, xanthation continues due to the excess carbon disulfide in the system. However, the net rate of xanthation is decreased due to the factors mentioned above. In addition, a redistribution of the xanthate groups takes place, resulting directly in a more uniform distribution of the groups with regard to chain length. This latter phenomenon has been referred to in the literature<sup>4</sup> as transesterification. Some question exists as to whether this is the actual

mechanism, since transesterification between cellulose chains appears to be quite improbable.

A complete understanding of the mechanism involved in emulsion xanthation of cellulose would require a thorough analysis of the kinetics involved in the above reactions. Quite understandably such a system is considerably more complicated than that encountered in the preparation of other common cellulose derivatives.

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### Synopsis

Viscose-grade cotton linters ( $\overline{DP}_w = 1135$ ) were converted to viscose by the emulsion xanthation technique. Two variables—namely, substitution level and xanthation time—were considered insofar as their influence on the uniformity of substitution with regard to chain length was concerned.

The stable diethylacetamide derivatives were prepared by reaction with diethylchloroacetamide and fractionally precipitated from aqueous 2-chloroethanol. The  $\overline{DP}_w$  and degree of substitution (DS) of the individual fractions were determined. The results in each case indicated that the longer chains were more highly substituted than the shorter chains. For a constant xanthation time (6 hr.), uniformity in substitution improved with increasing substitution level. For a constant  $CS_2$ :cellulose ratio (1.48), uniformity increased with xanthation time. A mechanism is suggested which accounts for these phenomena.

### Résumé

Des fils de coton pour viscose ( $\overline{DP}_w = 1135$ ) ont été transformés en viscose par xanthogénéation en émulsion. Les deux variables, à savoir le degré de substitution et la durée de xanthogénéation, étaient considérées dans la mesure où elles influencent l'uniformité de substitution le long de la chaîne. Les dérivés stables du diéthylacétamide ont été préparés par réaction avec le diéthylchloroacétamide et précipités par fractionnement à partir de 2-chloroéthanol aqueux. Le  $\overline{DP}_w$  et D.S. des fractions individuelles ont été déterminés. Les résultats dans chaque cas indiquent que les plus longues chaînes ont été substituées plus considérablement que les plus courtes. Pour un temps de xanthogénéation constant (c.à.d., 6 heures) l'uniformité de substitution s'améliorait avec un degré de substitution croissant. Pour un rapport constant  $CS_2$ :cellulose (1.48) l'uniformité croissant avec le temps de xanthogénéation. Un mécanisme a été proposé pour expliquer ces phénomènes.

### Zusammenfassung

Baumwollinters von geeigneter Qualität ( $\overline{DP}_w = 1135$ ) wurden nach dem Emulsions-Xanthogenierungsverfahren zu Viskose umgesetzt. Zwei Variable—nämlich der Substitutionsgrad und die Xanthogenierungsdauer wurden in Hinblick auf ihren Einfluss auf die Einheitlichkeit der Substitution in Abhängigkeit von der Kettenlänge untersucht. Das stabile Diäthylacetamidderivat wurde durch Reaktion mit Diäthylchloroacetamid dargestellt und aus wässrigem 2-Chloräthanol fraktioniert gefällt.  $\overline{DP}_w$  und D.S. der einzelnen Fraktionen wurden bestimmt. In jedem Fall zeigten die längeren Ketten eine höhere Substitution als die kürzeren. Bei konstanter Xanthogenierungsdauer (sechs Stunden) nahm die Einheitlichkeit der Substitution mit wachsendem Substitutionsgrad zu. Bei einem konstanten Verhältnis  $CS_2$ :Cellulose (1,48) nahm die Einheitlichkeit mit der Xanthogenierungsdauer zu. Ein Mechanismus zur Erklärung dieser Erscheinungen wird angegeben.

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