Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Evaluation of Pulps, Rayon Fibers, and Cellulose Acetate by GPC and Other Fractionation Methods

W. J. Alexander[a]; T. E. Muller[a]
[a] EASTERN RESEARCH DIVISION ITT RAYONIER, INC., WHIPPANY, NEW JERSEY

To cite this Article Alexander, W. J. and Muller, T. E.(1971) 'Evaluation of Pulps, Rayon Fibers, and Cellulose Acetate by GPC and Other Fractionation Methods', Separation Science and Technology, 6: 1, 47 — 71
To link to this Article: DOI: 10.1080/00372367108055551
URL: http://dx.doi.org/10.1080/00372367108055551

SEPARATION SCIENCE, 6(1), pp. 47–71, February, 1971

Evaluation of Pulps, Rayon Fibers, and Cellulose Acetate by GPC and Other Fractionation Methods*

W. J. ALEXANDER and T. E. MULLER

EASTERN RESEARCH DIVISION
ITT RAYONIER, INC.
WHIPPANY, NEW JERSEY 07981

Summary

Chain length distribution of a broad spectrum of wood celluloses and cellulose derivatives was determined by gel permeation chromatography. Relative amounts of short and long chain-length species were characterized, and uniformity indices were calculated. Prefractionation was found to be a desirable approach to amplify low- and high-DP regions. This was accomplished using a 55/45 ethyl acetate/ethyl alcohol mixture to yield the low-DP fraction and with a varying composition acetone/water system to obtain high-DP material. Fractions of regenerated cellulose from rayon obtained by treatment with 6.5 and 10% sodium hydroxide and by acid hydrolysis were characterized. Wood celluloses and rayons were analyzed in their nitrate form, whereas cellulose acetates were studied directly. This work was aimed primarily at elucidating the gel fraction that appears in the form of a peak of apparently high-DP material, resulting in a bimodal distribution.

INTRODUCTION

The application of gel permeation chromatography (GPC) to the molecular weight fractionation of wood cellulose, using the trinitrate derivative, was first reported in 1966 (*1*). There have since been a number of papers dealing with cellulose derivatives demonstrating growing interest in the use of GPC for cellulose analysis (*2–7*).

* Presented at the ACS Symposium on Gel Permeation Chromatography sponsored by the Division of Petroleum Chemistry at the 159th National Meeting of the American Chemical Society, Houston, Texas, February, 1970.

† Contribution No. 115 from the Research Divisions of ITT Rayonier, Inc.

A prime objective of this work was to define real differences in chain length uniformity between various grades of unmodified cellulose and the resultant end-products. This paper deals with the resolution of differences in the degree of polymerization (DP) distribution of wood pulp, rayon, fiber, and cellulose acetate as measured by GPC directly or on prefractionated samples. Numerical criteria have been selected for a variety of celluloses to permit evaluation of their relative DP uniformity for comparison with process history and various analytical characterizations.

Whereas relatively large and distinct differences in uniformity exist between paper-grade and dissolving-grade wood pulps, differences among dissolving grades may be small, primarily in average DP level. Small differences in the amount of short-DP material, however, are of major significance. Accordingly, particular emphasis was given to the characterization of regions at the extremes of polymer chain-length. The approach involved prefractionation by one of the conventional techniques used to isolate short and longchain-length fractions and their examination by GPC. With cellulose, as with other polymers, low molecular weight species are regarded as detrimental to physical strength while high molecular weight moieties influence the rheological behavior of polymers in solution.

EXPERIMENTAL

The work is divided into four groups. The first group outlines the experimental technique and calibration employed. The second group describes pulp analysis, the third relates to rayon fibers, and the fourth to cellulose acetates.

The main operating conditions employed are shown in Table 1. The chromatograph was a Waters Model 200 instrument, equipped with

TABLE 1

GPC Operating Conditions

Instrument: Waters Associates Model 200
Columns: Styragel 1×10^6, 3×10^6, 1×10^5, 3×10^4
Solvent: THF
Temperature: Ambient
Flow rate: 1 ml/min
Sample injection: Automatic
Refractometer null glass: 1/64 in.

four columns (2 columns of 10^6, 1×10^5, and a 3×10^4). The solvent was tetrahydrofuran (THF); flow rate 1 ml/min. Temperature was ambient, and a 1/64 in. null glass was used in the refractometer.

Pulps and rayons were analyzed after conversion to the trinitrate derivatives as reported previously (*3*). Cellulose acetates were in the conventional diacetate form with an acetyl level of 38–40%.

The amount of sample injected for a test was based on the DP level

TABLE 2

Schedule for Selection of Test Solution Concentration[a]

Concentration (g/100 ml)	DP Level
0.100	<1200
0.050	1200–2000
0.025	>2000

[a] Filtration apparatus: Hypodermic syringe, Swinny adapter. Media: Millipore Mitex (Teflon), Type MF-LS.

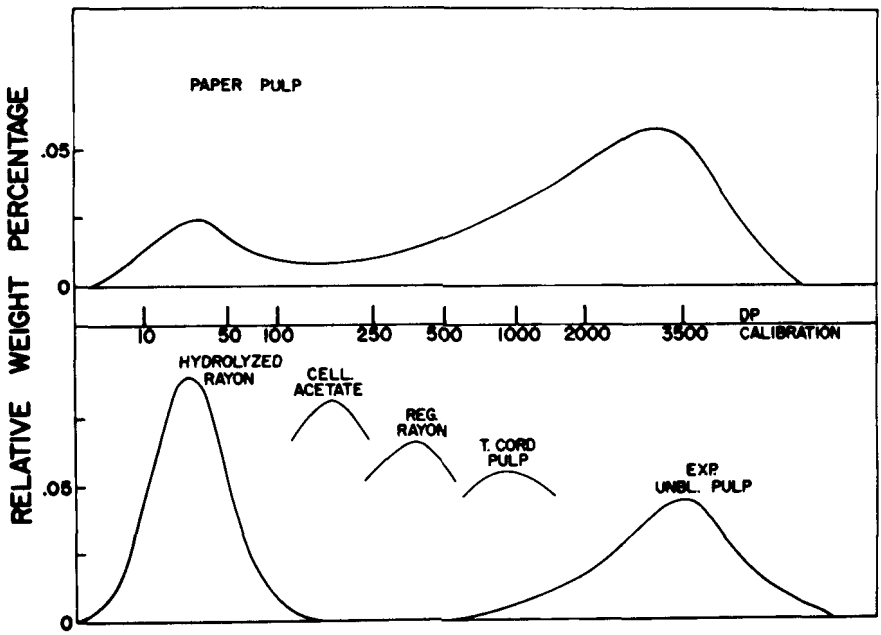

FIG. 1. Range in cellulose DP illustrated on DP scale employed.

of the material, as shown in Table 2. The volume of solution was 2 ml. An automatic sample injector was used for the most part.

RESULTS AND DISCUSSIONS

The DP range as applied to the actual GPC elution curves is shown in Fig. 1. With two exceptions which involve different columns, all figures showing elution curves have the same scale, ranging from 2 to >3500 DP. The top curve represents paper pulp, covering virtually the entire DP range. The bottom curve is intended to place in perspective the various celluloses to be discussed, high-DP wood or cotton celluloses, dissolving pulps, rayon fibers, cellulose acetates, and hydrolyzed rayon which is referred to as levelling-off DP or LoDP cellulose. The scale shown in the center was arrived at from the calibration curve shown in Fig. 2.

Most of the points in Fig. 2 represent cellulose nitrate fractions separated by fractional precipitation of predominantly cotton cellulose. There are two exceptions; the members of lowest DP are cello-

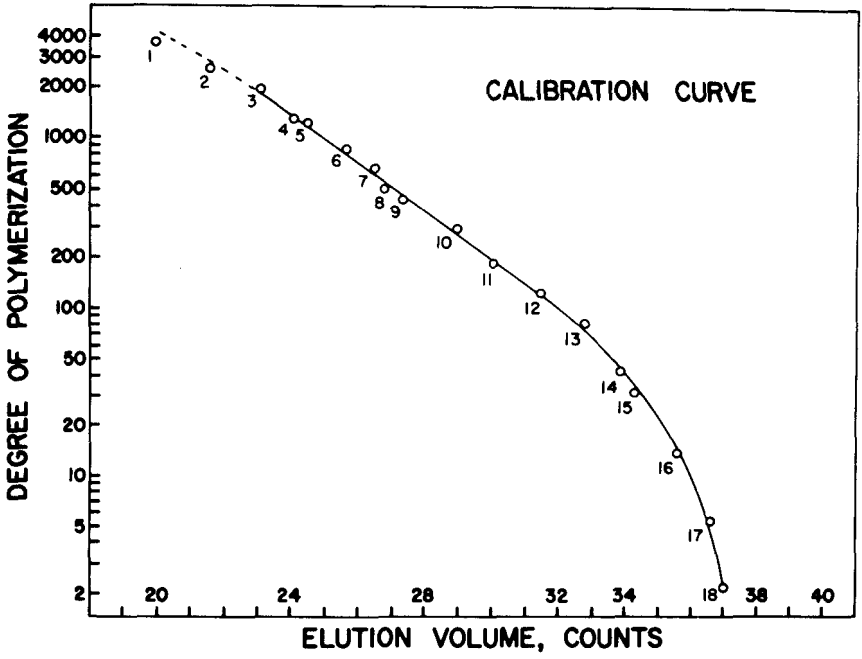

FIG. 2. GPC calibration curve.

pentose and cellobiose. The DP's given are nitrate DP values obtained from intrinsic viscosity determinations in ethyl acetate at 25°C (*8*).

Elution curves for fractions employed for the calibration are shown in Fig. 3. Nearly all of these tests were made using solutions with a concentration of 0.05 g/100 ml. Amplification was reduced for the narrow distribution cellobiose and cellopentose. The two highest DP fractions were analyzed at a concentration of 0.025 g/100 ml; these were obtained by fractionating selected celluloses into four or five fractions to cover the DP range.

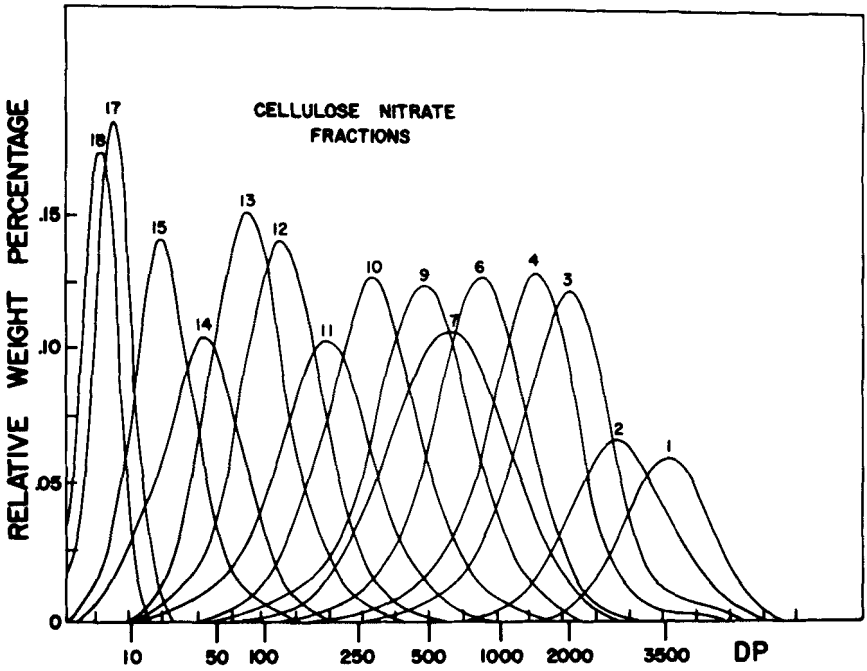

FIG. 3. GPC elution curves for cellulose nitrate fractions employed for calibration.

The prefractionation procedure is outlined in Table 3. Aliquots of water were added to the sample dissolved in a mixture of 91% acetone and 9% water. The amount of initial sample dissolved varied from 0.10 g for a 3000 DP cotton to 1.00 g for two celluloses obtained from aged alkali cellulose with average DP values below 100.

Figure 4 shows a series of celluloses obtained from aged alkali cellulose derived from wood pulp. A similar series was prepared from cot-

TABLE 3

Precipitation Fractionation Scheme for Cellulose Nitrate
Solvent: 91% acetone, 9% water
Amount: 200 ml
Nonsolvent precipitant: water

Sample weight (g)	DP Level
0.100	3000
0.150	2000
0.300	1000
0.500	250
1.000	100

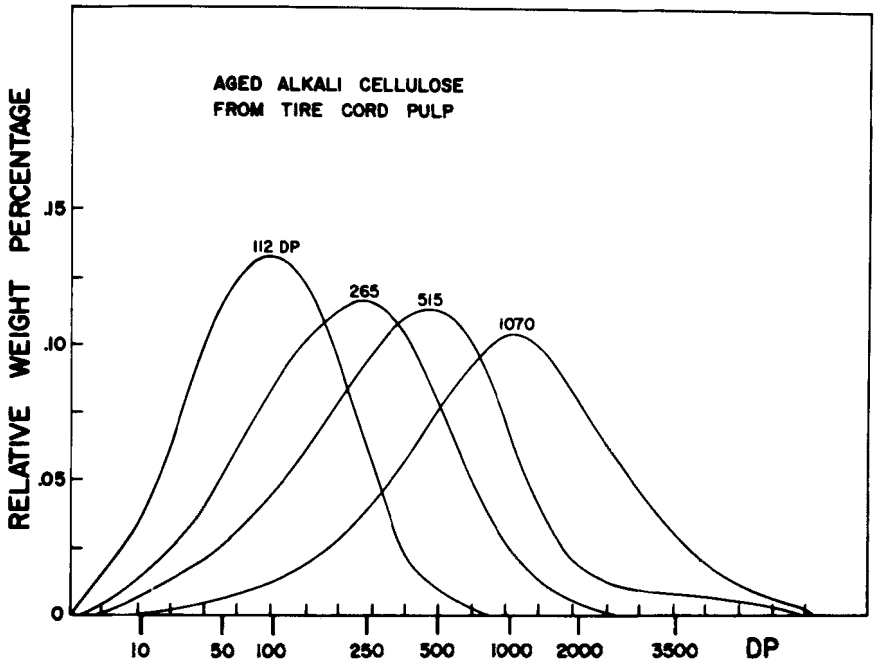

FIG. 4. GPC elution curves for aged alkali cellulose.

ton linters to provide samples for fractionation to calibrate in the DP range below 600.

Figure 5 shows curves for the fractions of one of these samples with an average DP of 77, from which calibration points corresponding to 120, 80, and 40 DP were obtained.

The next group of figures illustrates differences among the chain-length distributions of a variety of wood pulps.

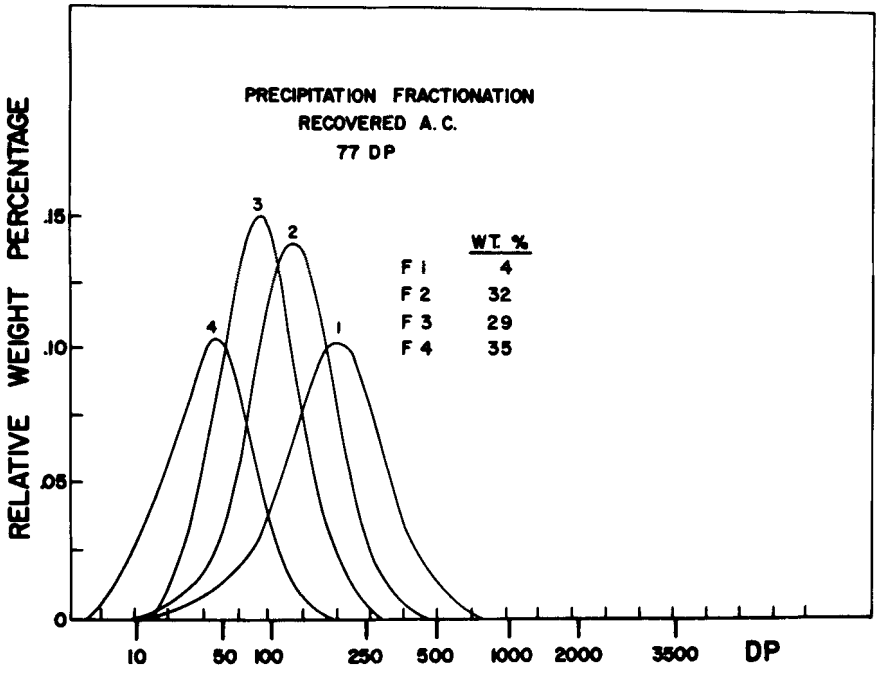

FIG. 5. GPC elution curves for cellulose nitrate fractions from low DP recovered alkali cellulose.

Figure 6 depicts three sulfite pulps. Numbers 1 and 2 are paper pulps which have virtually the same hemicellulose content. The fraction soluble in 10% sodium hydroxide at 20°C (S_{10}) is 13%. This percentage corresponds approximately to that portion classified as <100 DP by the GPC curve. A 10% difference in average DP level (the principal difference between these pulps) appears primarily in very high DP material. Pulp No. 3 is a low-average-DP pulp in which a high percentage of the hemicellulose component was retained as in the paper pulps. The location of the hemicellulose peak is shifted from

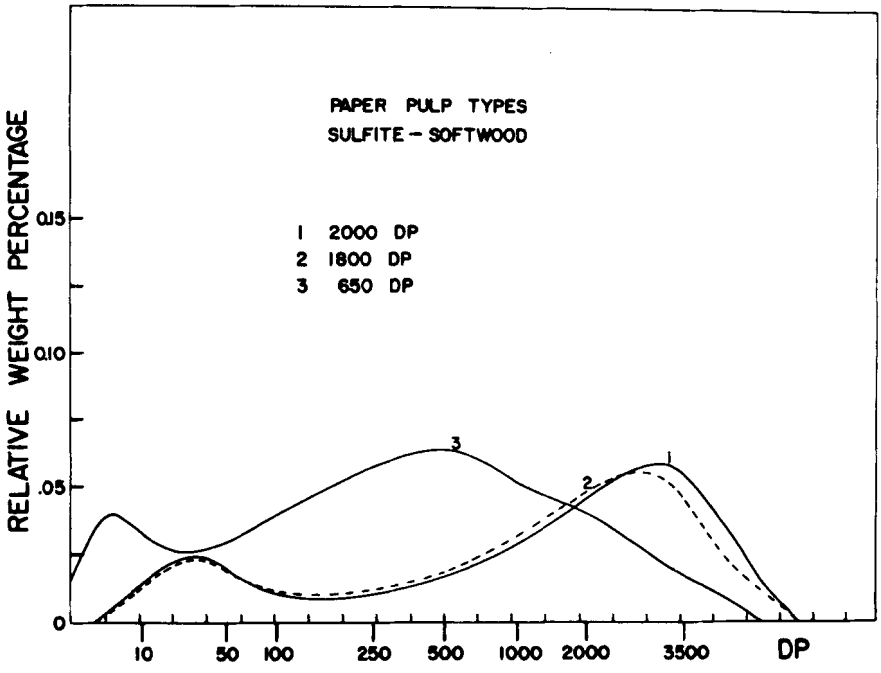

FIG. 6. GPC elution curves for three softwood paper pulp types.

DP 50 to the less than 25 DP level. The fraction classified by GPC as <100 DP has been increased to 24%, corresponding to a S_{10} value of 23.8%. A larger area under the curve for Pulp 3 may be accounted for by the solution concentration used (0.1% vs. 0.05%) for Pulps 1 and 2.

Figure 7 shows curves for two kraft paper pulps. The wood source for one was a blend of southern pine and hardwoods in which pine is the major component. The other one is 100% hardwood. These pulps have a distinct third peak at the high-DP end of the scale in addition to peaks representing the main cellulose and hemicellulose portions. This peak appears at the exclusion volume of the columns and is considered to be the result of a "gel fraction." This is not evident in the curves for the pulps shown in the previous figures. A significant difference in xylan content exists among these pulps. The hardwood pulp contains 16% xylan, the predominantly pine pulp 7%, while the pulps discussed previously had 2% or less. Some correlation seems to be implied between gel fraction and xylan residue. The residue may nitrate

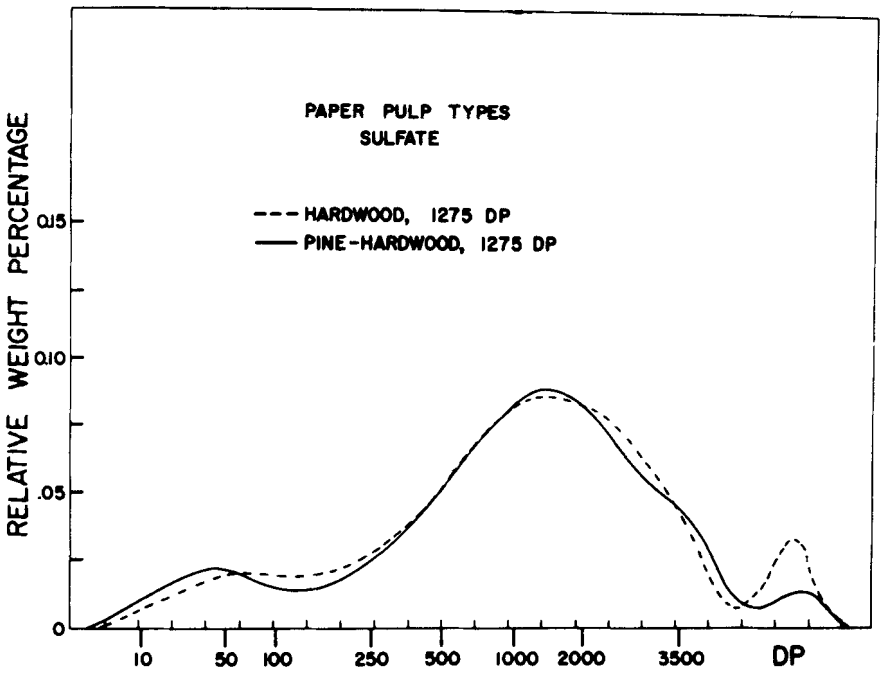

FIG. 7. GPC elution curves for two sulfate paper pulps containing hardwoods.

to the dinitrate but not to the trinitrate derivative. The extent and exact nature of this connection will be the subject of a separate study.

Figure 8 depicts four dissolving grade pulps. Listing these in the order of decreasing average DP, they are: acetate-, tire cord-, rayon staple-, and cellophane-grade pulps. The curves reflect differences in the content of short-DP material among these pulps; the tire cord and acetate grades show the least and the cellophane grade pulp the most. Three factors may be obtained from the GPC curves giving numerical values for establishing distribution uniformity. These values are relative areas under the curve corresponding to specific DP classifications: (a) the percentage of <50 DP and (b) of <100 DP material to evaluate low-DP content, and (c) the percentage >2 times ($2\times$) the average DP to reflect differences in high-DP material.

Table 4 lists values obtained by this procedure for these four pulps. The figures for amount of <100 DP material correspond roughly to the respective S_{10} levels and reflect a low amount of short-chain-

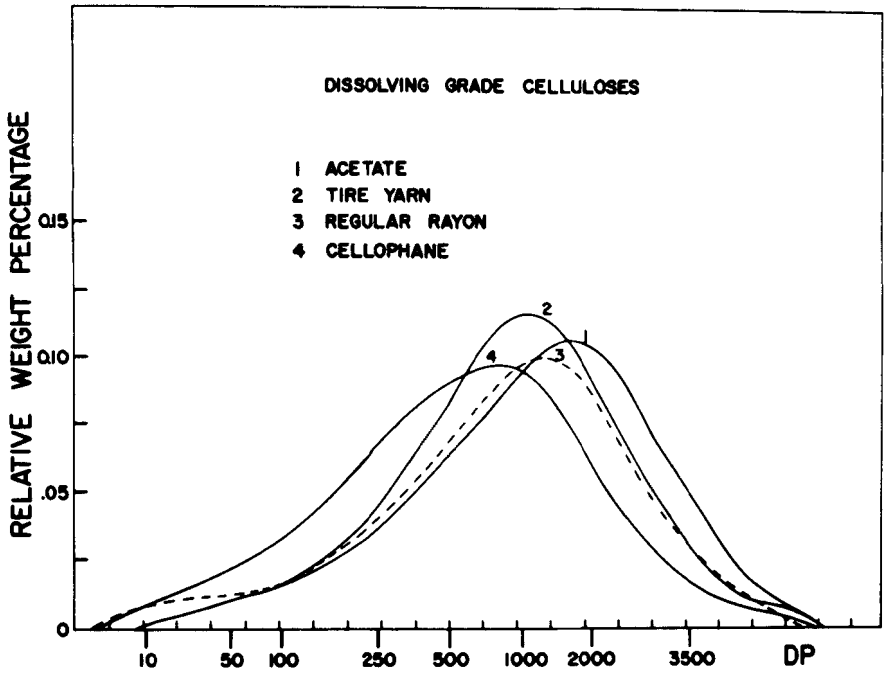

FIG. 8. GPC elution curves for several grades of dissolving grade celluloses.

length material present in top quality tire cord and acetate pulps. The percentages of "$>2\times$ average-DP" material fall within a relatively narrow range for these dissolving pulps. This is not characteristic of all pulps, as shown in Table 5. This table lists DP uniformity data for several types of celluloses at the 700 average-DP level. The last column gives the percentages classified by GPC as $>2\times$ average-DP, showing a range from 11 to 39. Although S_{10} values are not listed,

TABLE 4

Comparison of DP Uniformity Indices for Several Dissolving Grade Celluloses

Pulp type	% <50 DP	% <100 DP	% >2 × DP avg
Tire-cord grade	1.3	3.2	22
Acetate grade	1.4	3.3	23
Rayon grade	3.7	6.4	24
Cellophane grade	4.5	8.6	24

TABLE 5

Comparison of DP Uniformity Indices for Several Celluloses at 700 DP Level

Cellulose	DP	% <50 DP	% <100 DP	% >2 × DP avg
Recovered alkali cellulose viscose linters	700	1.3	4.2	11
Recovered alkali cellulose wood pulp	700	2.5	6.2	18
Wood pulp cellophane grade	760	4.5	8.6	24
Wood pulp experimental	760	5.6	10.1	39

there is a reasonable correlation between the S_{10} level and the <100 DP material. GPC curves for three of these celluloses are shown in Fig. 9.

Direct comparison of the curves is possible because of the similarity in DP level. It is quite apparent that there is a difference in the per

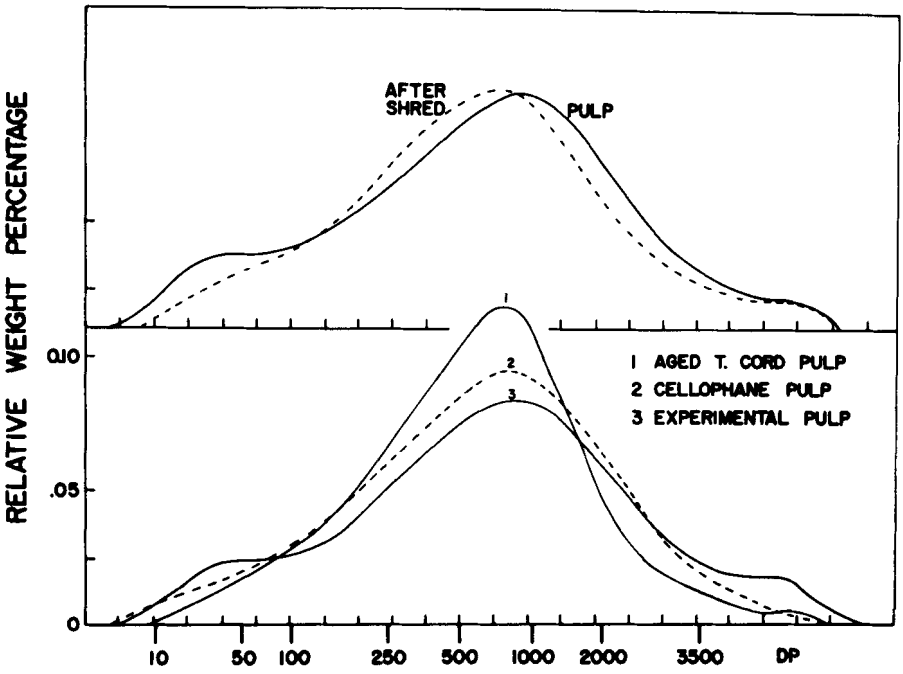

FIG. 9. GPC elution curves for three 700 DP celluloses (lower curves) and pulp before and after steeping and shredding steps in viscose process.

cent material classified as <100 DP and >2× average-DP. The upper set of curves shows the effect of steeping an experimental pulp in 18% sodium hydroxide on its chain-length distribution; there is an indication of the removal of some low-DP material. With more highly refined pulps this effect of steeping is hardly noticeable.

A single-stage fractional extraction of nitrated cellulose was carried out to permit a closer examination of the low-DP components. The conditions for the fractionation scheme employed are given in Table 6. The fractionation involves a 48-hr extraction of the cellulose nitrate with a mixture of 45% ethanol (95%) and 55% ethyl acetate at ambient temperature.

GPC fractions obtained from three prefractionated pulps are shown in Fig. 10. Curves 1 and 1R represent soluble and insoluble fractions from an experimental, high-DP, high-hemicellulose pulp. The two components represent a distinct separation of the hemicellulose fraction from the cellulose. The curves show almost no material present in the DP range of 250 to 750.

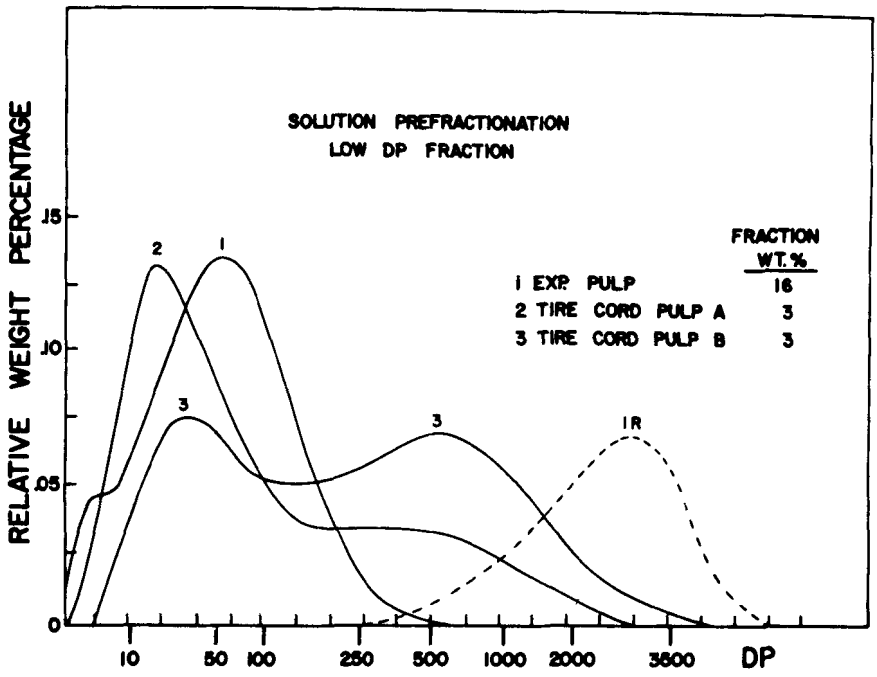

FIG. 10. GPC elution curves for low DP fractions isolated by prefractionation—broad range GPC columns.

TABLE 6

Single-Stage Solution Fractionation Scheme for Cellulose Nitrate

Solvent: 45% ethanol (95%), 55% ethyl acetate
Amount: 200 ml
Sample wt: 2.00 g
Extraction: 48 hr at ambient temperature
Filtration: Sintered glass funnel
Solute recovery: Aliquot evaporated in water bath

Curves 2 and 3 represent the low DP fractions (3% by weight), isolated from two dissolving pulps with an average DP of 1100. The principal difference between these two highly refined pulps is that No. 3 had received a cold caustic extraction to reduce low-DP material. Two points may be noted: (a) extraction with cold caustic did reduce the percentage of material classified as <100 DP, and (b) it increased accessibility, allowing the extraction of a higher percentage of longer (>100 DP) chains.

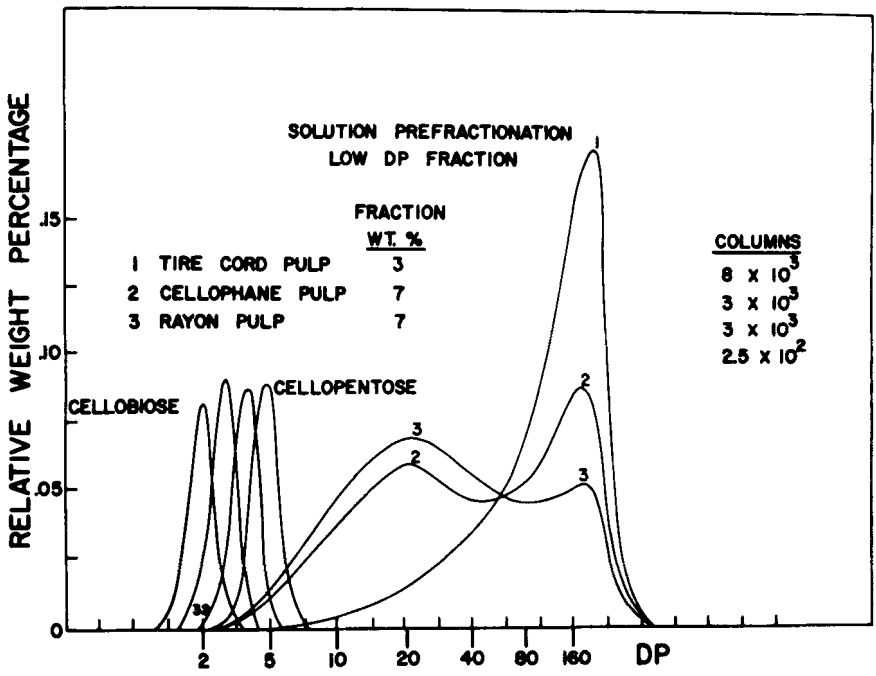

FIG. 11. GPC elution curves for low DP fractions isolated by prefractionation—low DP range GPC columns.

Curves obtained for low DP fractions isolated from tire-cord-, cellophane-, and rayon-staple-grade pulps are compared in Fig. 11. These curves were obtained using a set of columns selected for lower DP celluloses. The calibration scale covers the 2 to 160 DP range. Resolution of cellobiose, cellotriose, cellotetrose, and cellopentose is shown by the peaks on the left. Extraction isolated a fraction 7% by weight from the cellophane and rayon pulps and only 3% from the tire-cord pulp. The chain-length composition differs among the three fractions. The rayon-pulp fraction has the highest percentage at the 25 DP level and the highest S_{18} or gamma values. The cellophane-pulp fraction shows a higher percentage at the 150 DP level than does the rayon fraction. The S_{10}–S_{18} percentage (or beta fraction) is the highest for this pulp. The fraction isolated from the tire-cord pulp represents only 3% of the pulp by weight, it is almost free of material in the <25 DP range, and it has a substantial amount of >100 DP material.

An abridged version of the ASTM fractional precipitation method

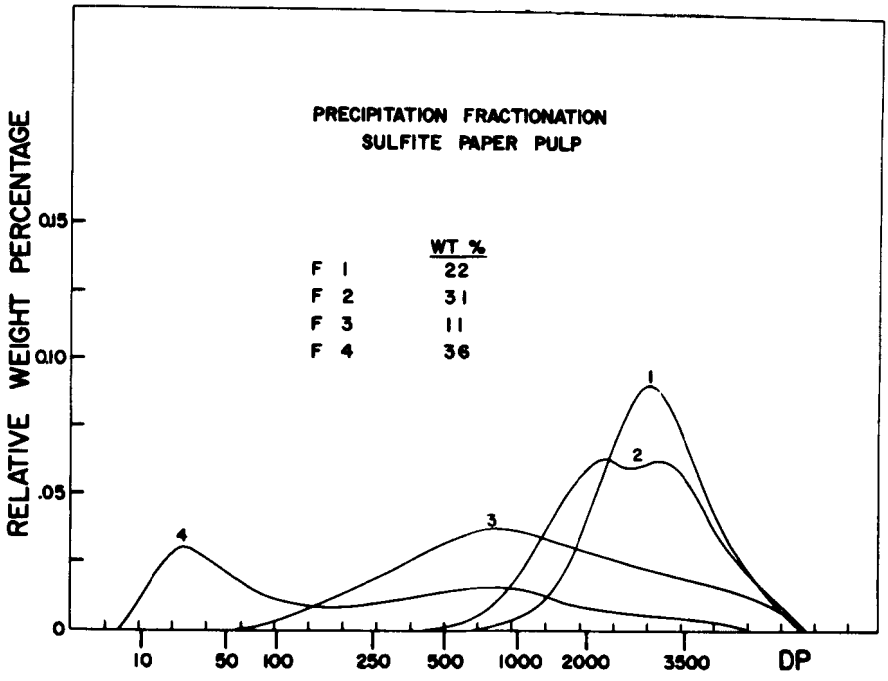

FIG. 12. GPC elution curves for precipitation fractions from sulfite paper pulp.

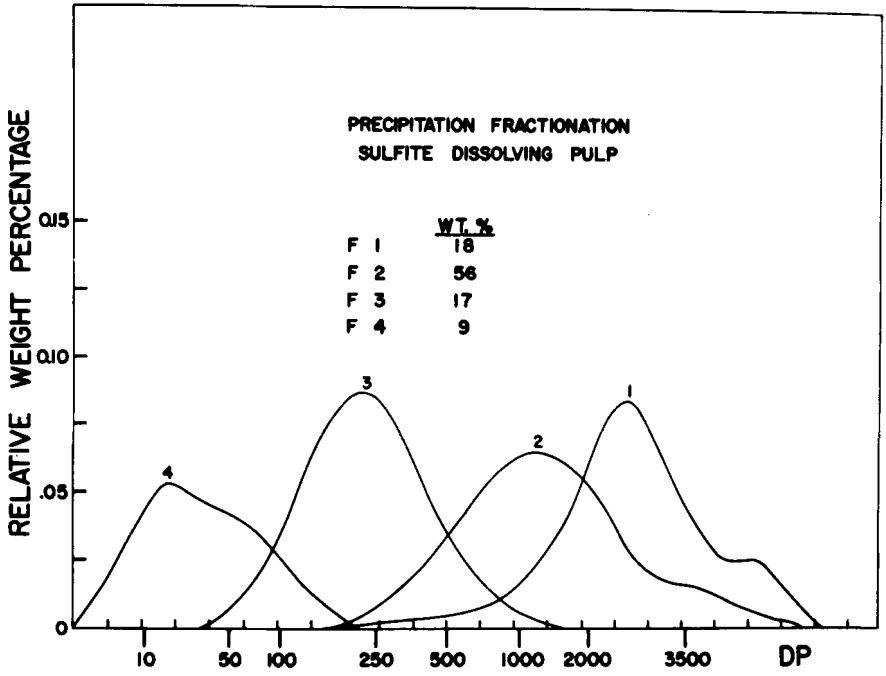

FIG. 13. GPC elution curves for precipitation fractions from sulfite dissolving pulp.

for cellulose nitrate was used to permit examination of high-DP portions in greater detail. The technique proved to be useful at the two extremes of the DP range.

Figure 12 shows separation of a 2000-DP paper pulp into four fractions. The No. 1 fraction has a symmetrical distribution peaking at about 3000 DP. The No. 4 fraction contained essentially all of the hemicellulose components.

Figure 13 shows curves representing fractionation of a 1250-DP sulfite dissolving pulp. The No. 1 fraction contains 18% of the sample and has a shoulder or the beginning of a second peak. The No. 4 fraction represents 9% of the sample and is comprised primarily of chains <100 DP.

Figure 14 compares the first precipitated fractions from a sulfate hardwood paper pulp, a sulfite paper pulp and a 2000-DP cotton linters. The linters and sulfite-paper-pulp fractions have similar distributions, neither one having a gel fraction. The sulfate hardwood

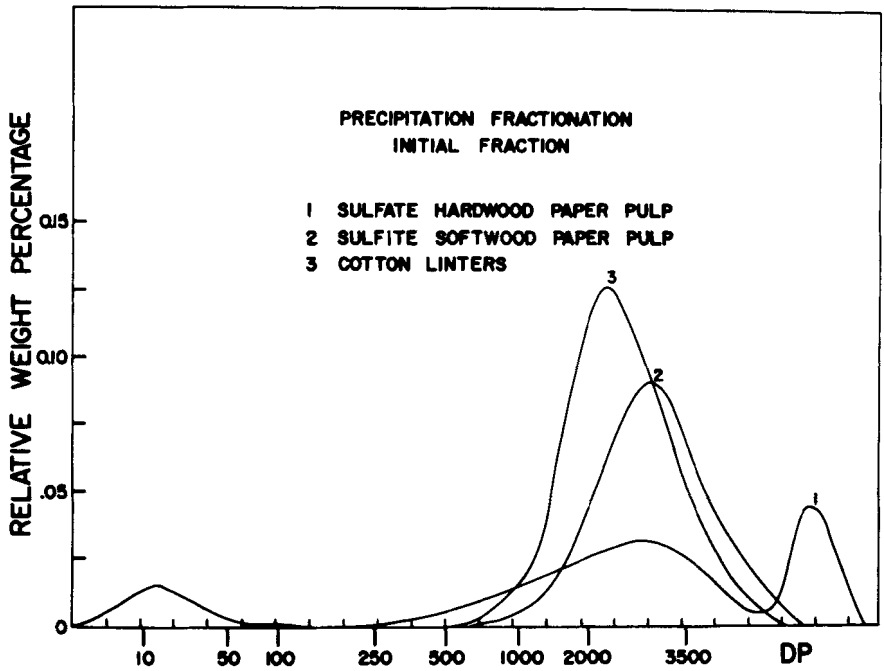

FIG. 14. GPC elution curves for initial precipitation fraction from three pulps.

paper-pulp fraction is rather unique in that it shows that this particular fraction did not separate according to DP, but according to solubility differences attributable to other factors. The exclusion volume component apparent in the unfractionated pulp is shown to be concentrated in the first two fractions. In previous studies, analyses of denitrated fractions separated by the same procedure applied to pulps with a high xylan content revealed the major portion of xylan to fractionate in the first two fractions.

Figure 15 compares the DP distribution of four regenerated cellulose fibers: regular rayon (No. 1), a polynosic rayon (No. 2), Fortisan (No. 3), and a high-wet-modulus (HWM) type (No. 4). The latter fiber has an average DP over two times that of the regular rayons. The percentage classified by GPC as <100 DP ranges from 19% for the regular rayon to 8% for the Fortisan and the Experimental High Performance-type (No. 4), Table 7. Relatively large differences between the high-DP regions of the curves are evident. For example,

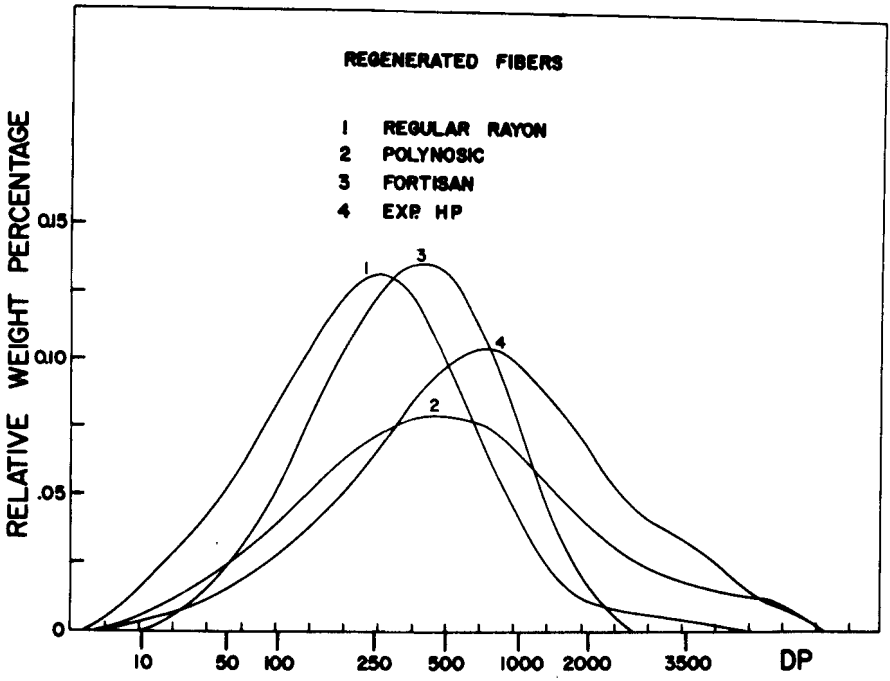

FIG. 15. GPC elution curves for several types of regenerated cellulose fibers.

a value of 28 was obtained for the >2× average-DP for the polynosic, compared to values of 15 for the Fortisan and regular rayon samples.

Data for these fibers and a tire yarn examined by GPC are shown in Table 8. The fibers range from 300 in average DP for regular rayon to 700 for an improved high performance, HWM type. Their resist-

TABLE 7

Comparison of DP Uniformity Indices for Regenerated Cellulose Fibers

Type	DP	% <50 DP	% <100 DP	% >2 × DP avg
Regular rayon	300	10	19	15
Tire yarn	525	4	9	18
Polynosic	500	5	11	28
Exp. HP	700	3	8	18
Fortisan	400	3	8	15

TABLE 8

Analytical Data for Regenerated Cellulose Fibers

	Regular rayon	Polynosic staple	Exp. HP staple	Tire yarn	Fortisan
DP	300	500	700	525	400
Caustic solubility					
$S_{6.5}$, %	23.5	8.3	1.8	19.5	0.6
S_{10}, %	50.0	20.2	13.8	50.0	2.8
Acid hydrolysis					
Limit I.V. (cuene)	0.19	0.26	0.28	0.17	0.28
Yield, %	84.6	92.0	94.0	88.7	92.8

ance to caustic varies as indicated by the respective solubilities in 6.5 and 10% sodium hydroxide, ranging from <1 to 50%. Yield and leveling-off intrinsic viscosity data for cellulose residues obtained from these fibers after a standardized acid hydrolysis treatment are in-

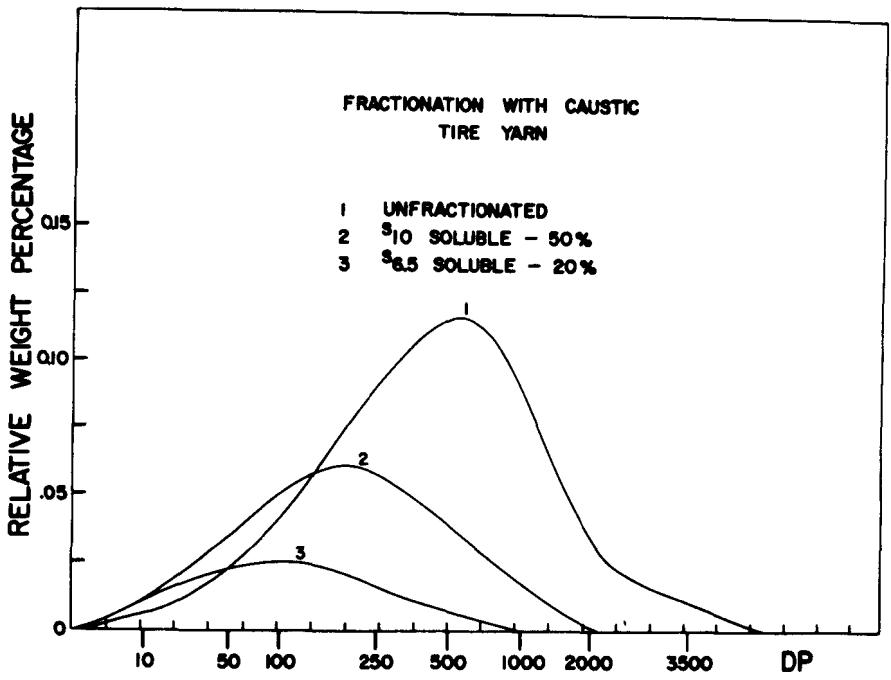

FIG. 16. GPC elution curves for tire yarn and caustic-soluble fractions.

cluded. GPC analysis has been combined with caustic solubility and acid hydrolysis to gain a better appreciation of their meaning and significance.

With pulps, the amount soluble in 10% sodium hydroxide correlates approximately to the percentage classified as <100 DP. This does not follow for regenerated fibers which are far more susceptible to swelling in caustic. For example, 50% of a regular-type rayon or a conventional tire yarn may be dissolved in 10% sodium hydroxide while the soluble fraction of HWM types may be less than 10%. The resistance to caustic solution, particularly to 6.5% sodium hydroxide at 20°C, has proved to be a useful technique for classifying fibers. The HWM types, in which crystallite regions are relatively large and more highly oriented, are characteristically more resistant to sodium hydroxide.

Figure 16 shows the DP distribution of $S_{6.5}$- and S_{10}-soluble fractions of a tire yarn fiber. The relative areas of the two fractions have been adjusted by selecting concentrations to correspond to the relative

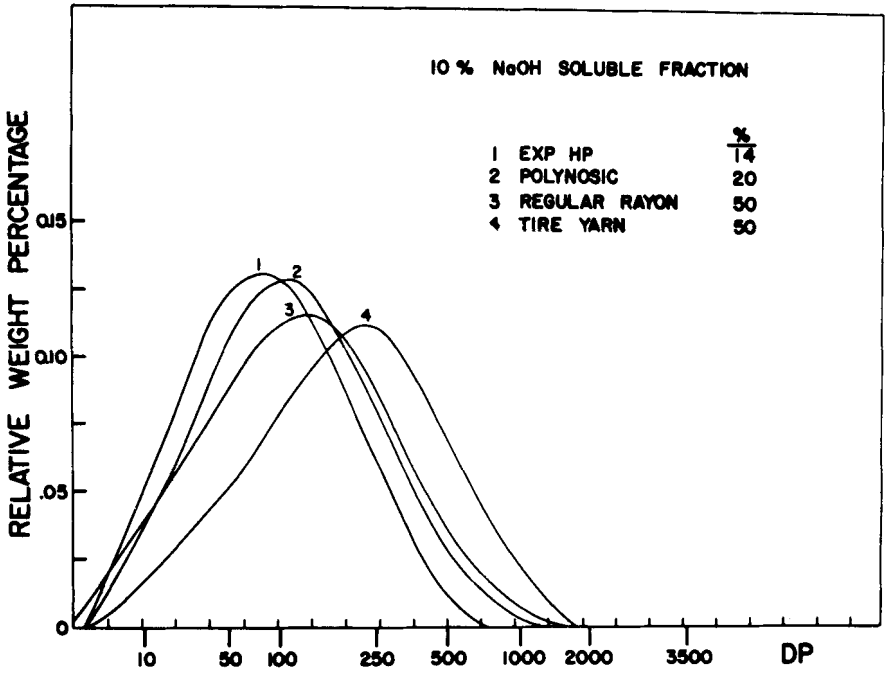

FIG. 17. GPC elution curves for 10% NaOH-soluble fraction from four types of rayon fiber.

weight percentages. It is evident that caustic fractionation is controlled by fiber accessibility as well as DP. A more concentrated caustic solution has extracted more and longer chains. A number of fibers have been examined in this manner, and they were found to follow a similar pattern with shifts on the scale corresponding to variations in average-DP level or the amount of caustic-soluble material.

Direct comparison of the S_{10} fraction from the four fibers is shown in Fig. 17, indicating a difference in average-DP level. The lower-DP sample is from the HWM fiber from which the lowest weight-percentage was dissolved. The fraction with the highest-DP represents the tire yarn fiber with the highest weight-percentage soluble in 10% sodium hydroxide.

Leveling-off DP celluloses obtained by subjecting rayon fibers to a standard acid hydrolysis treatment show differences in the DP of the acid-resistant residues. These differences may reflect, to some degree, the relative size of the crystallite or most highly oriented regions of

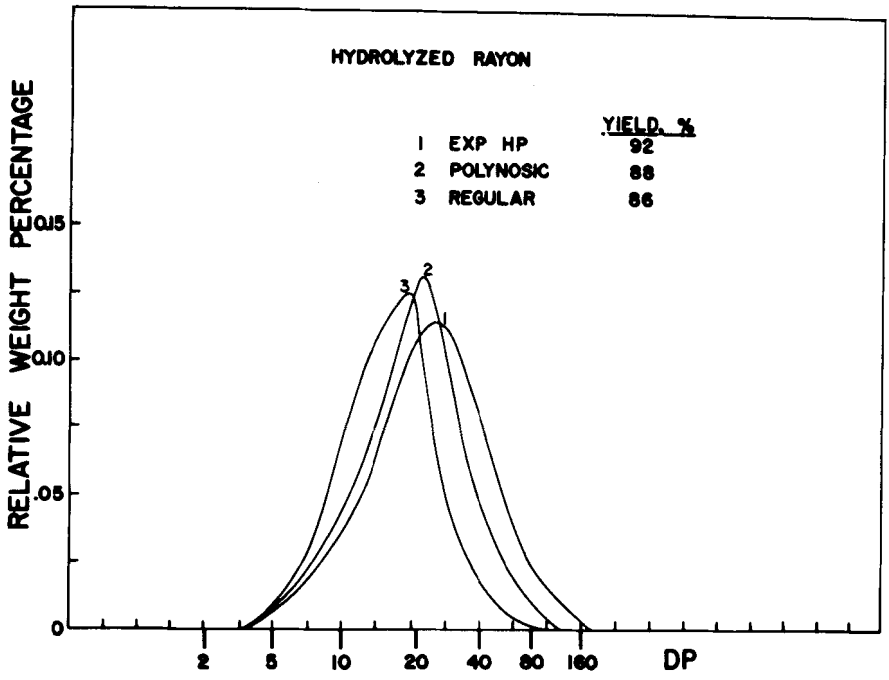

FIG. 18. GPC elution curves for hydrolyzed rayon—limit or leveling-off DP cellulose residues.

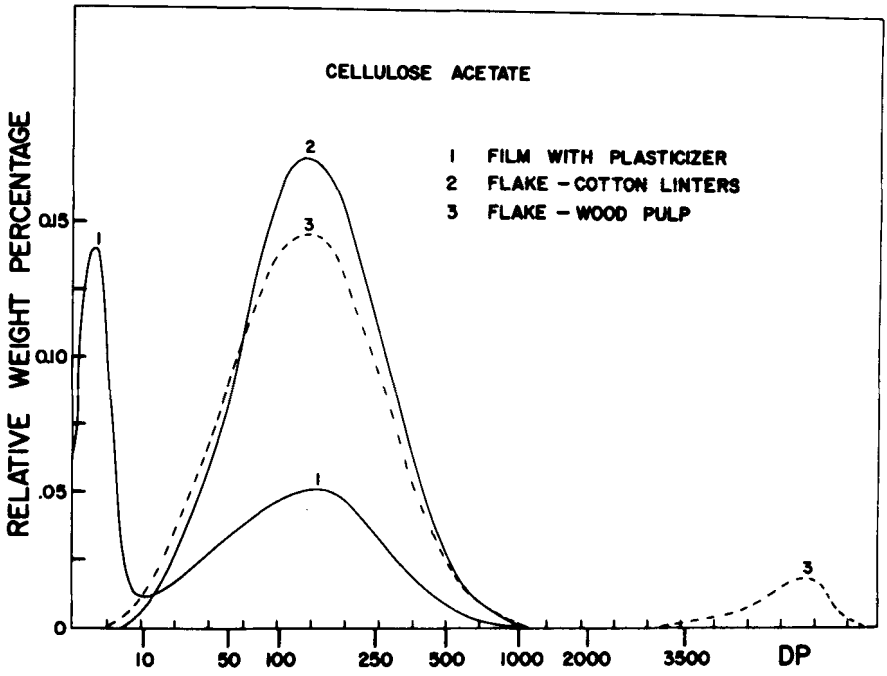

FIG. 19. GPC elution curves for cellulose acetates.

the fiber. Although the DP levels are low (in the 20 to 30 DP range), the LoDP cellulose from HWM fibers may have an average DP of 50% or more, greater than that from a regular rayon or conventional tire yarn.

Figure 18 compares the curves of three hydrolysis residues representing a high-performance, HWM fiber (No. 1), polynosic (No. 2), and a regular rayon (No. 3). These were obtained on the columns selected for low DP celluloses.

The balance of this work relates to cellulose acetates. Figure 19 compares a plasticized acetate film and acetate flakes derived from cotton linters and from wood pulp. In Curve 1 the low molecular-weight plasticizer is resolved as a distinct peak. Curves 2 and 3 show cotton and wood pulp acetates to have a similar DP distribution. However, Curve No. 3 from wood pulp shows a small peak at the exclusion volume of the columns. This peak was also designated the "gel fraction."

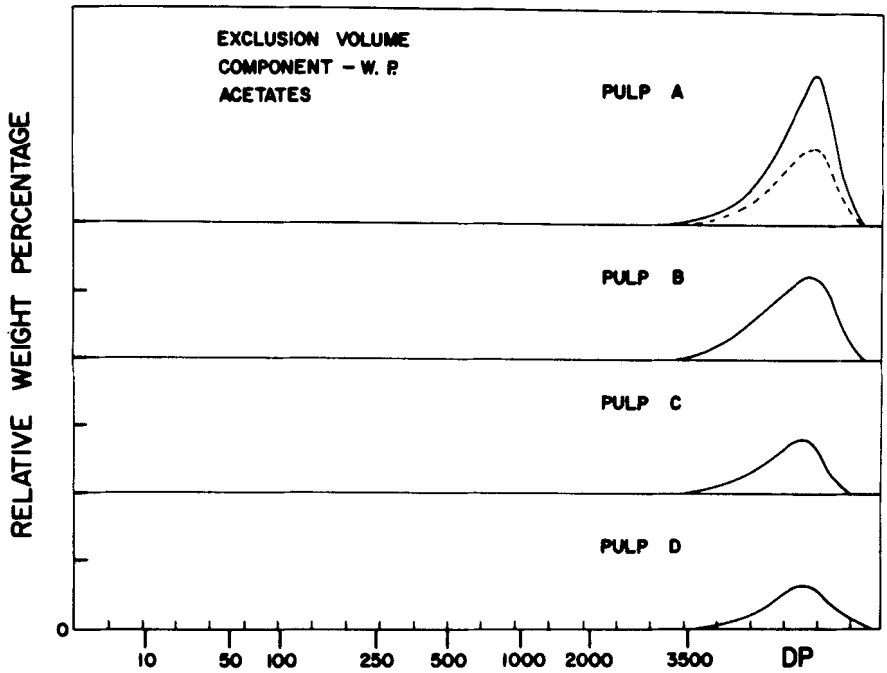

FIG. 20. GPC elution curves for gel fraction component in several wood pulp acetates.

The relative size of this fraction may vary with the pulp grade from which the acetate is derived, as shown in Fig. 20. The size of the gel fraction is smaller in acetates derived from more highly purified grades of pulp. Pulps A through D represent acetate grades containing progressively less hemicellulose. The dotted curve for Pulp A shows a reduction in the gel fraction in the GPC test solution, resulting from substituting a Krueger filter pad for the Millipore Mitex filter that was generally employed in preparing the GPC test solutions.

The "gel fraction component" is removed in the first (least soluble) fractions isolated by precipitation-fractionation of the acetate. Figure 21 shows curves obtained for fractions isolated from an acetate made from wood pulp. The fractionation scheme employed a solvent/nonsolvent system of acetone and water. The first fraction represented 3% and the second 15% of the sample. All of the gel fraction was removed in these two fractions. In previous studies where fractions were separated by the same method, the first one or two frac-

tions precipitated were found to account for the major portion of the xylan, mannan, and carboxyl present in the sample.

Figure 22 shows that the "gel fraction" is absent in the fractions obtained by precipitation from a cotton linters acetate.

Figure 23 compares the GPC curves of a cellulose acetate and of the nitrate derivative of this same sample after deacetylation. The nitrated sample peaks at a higher DP than the original one. It might be expected that after saponification with caustic and subsequent nitration there would be a slight shift to a lower DP level. It is more likely, however, that for a given DP the cellulose nitrate chain has a larger volume in THF than does the cellulose acetate. This would be consistent with their respective DP/intrinsic viscosity relationships. It also calls attention to the fact that the DP calibration used is not applicable to cellulose acetates without some adjustment. One additional point to note is the presence of a "gel fraction peak" in the

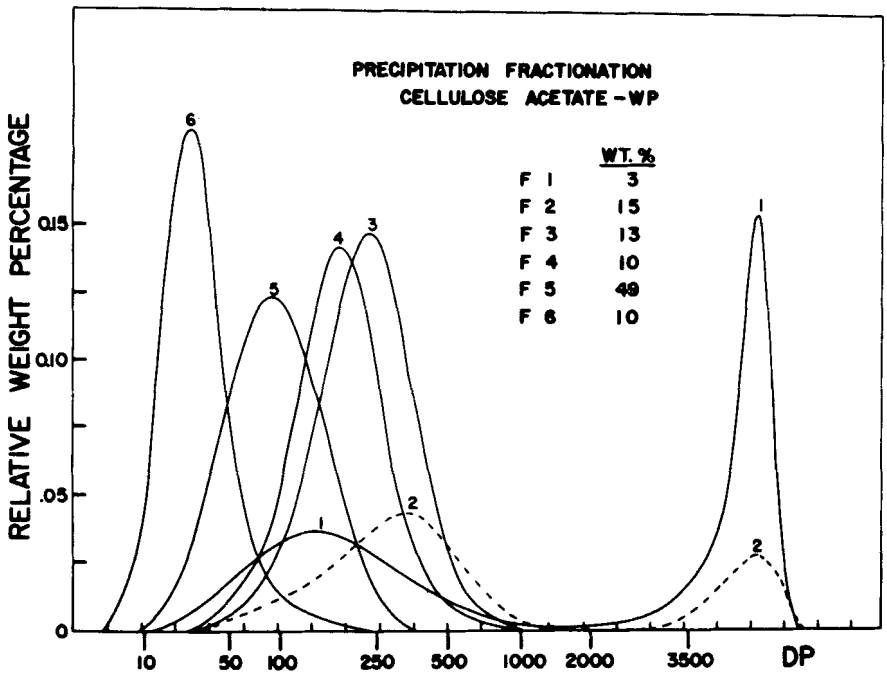

FIG. 21. GPC elution curves for cellulose acetate fractions from wood pulp.

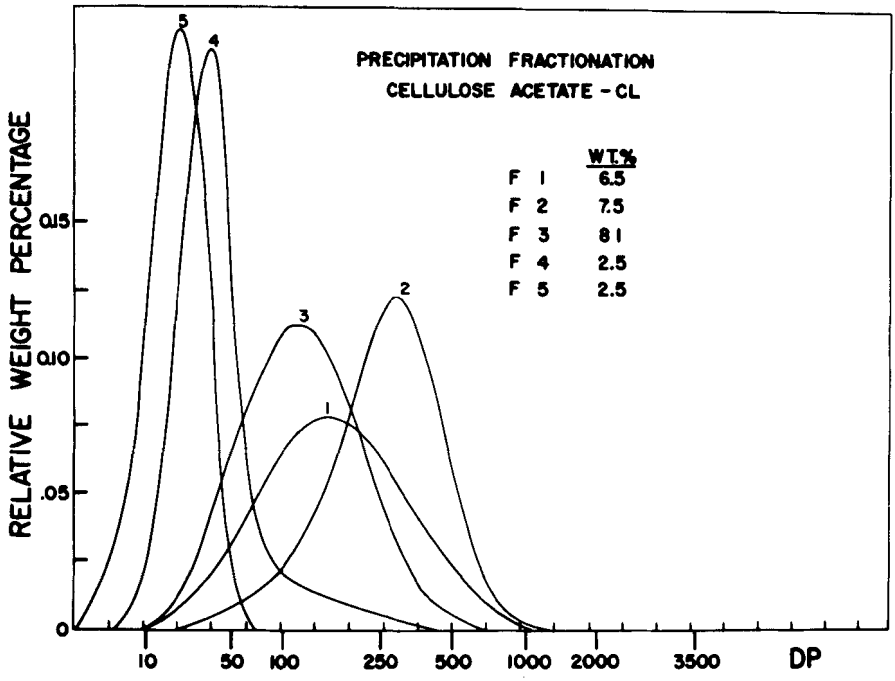

FIG. 22. GPC elution curves for cellulose acetate fractions from cotton linters.

nitrate sample not present in the acetate, suggesting that all gel fractions do not derive from a common origin.

CONCLUSIONS

Numerous cellulosic samples have been fractionated on a gel column system calibrated with cellulose nitrate fractions. These samples have been evaluated in terms of relative DP, and DP uniformity levels were compared. Conventional fractional-solution and fractional-precipitation methods have been utilized effectively in conjunction with GPC to improve the definition of the DP distribution of high- and low-DP portions isolated from pulps, rayon fibers, and cellulose acetates. GPC has made possible a clearer understanding of the DP distribution of celluloses than was previously available from other noninstrumental fractionation methods.

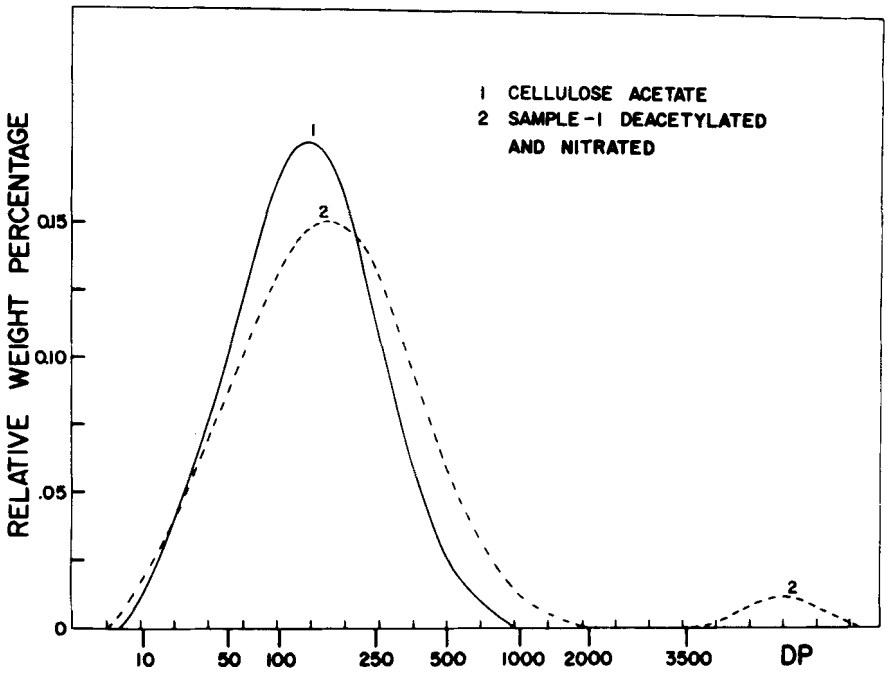

FIG. 23. GPC elution curves for cellulose acetate and the cellulose nitrate derivative of the saponified acetate.

REFERENCES

1. L. Segal, *J. Polym. Sci., Part B*, **4**, 1011 (1966).
2. G. Meyerhoff and S. Joranovic, *J. Polym. Sci., Part B*, **5**, 495 (1967).
3. W. J. Alexander and T. E. Muller, *J. Polym. Sci., Part C*, **12**, 283 (1968).
4. L. Segal, *J. Polym. Sci., Part C*, **21**, 267 (1968).
5. R. J. Brewer, L. J. Tanghe, S. Bailey, and J. T. Burr, *J. Polym. Sci., Part A-1*, **6**, 1697 (1968).
6. R. Y. M. Huang and R. G. Jenkins, *Tappi*, **52**, 1503 (1969).
7. L. Segal and J. D. Timpa, *Tappi*, **52**, 1669 (1969).
8. W. J. Alexander and R. L. Mitchell, *Anal. Chem.*, **21**, 1487 (1949).

Received by editor April 16, 1970