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Molecular Weight and Intrinsic Viscosity of Nitric Triesters of Corn Starches and Dextrins

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Introduction

It has been shown elsewhere[1] that starches and dextrins can be esterified to exceptionally high nitrogen content, approximating the theoretical triester, by means of nitrogen pentoxide. Anhydrous conditions and relatively low temperatures of nitration imply a minimum degree of degradation of the polysaccharide. It was accordingly postulated that this method of nitration might be useful as a new tool of structural investigation, working with unfractionated nitric esters, in non-aqueous solvents, very nearly completely esterified and substantially undegraded. The investigative method used was the determination of number average molecular weights, intrinsic viscosities,[2] and a study of the graphical relationship of these quantities through the modification of Staudinger's formula, as proposed by Mark.[3]

The polysaccharides studied were primarily corn starches and corn dextrins; although for purposes of comparison, cellulose, and corn and potato amyloses were included. A determination was also made of the intrinsic viscosity of maltose octanitrate, nitrated with nitrogen pentoxide. It was found that the simple Barger isopiestic method was suitable to molecular weight determinations of high polymers; that an apparent linear relation between molecular weights and intrinsic viscosities, obeying Mark's variation of Staudinger's formula, existed over an unusually wide range of molecular weights; that a graphical distinction was indicated between different types of modified starches; that the experimentally determined value for the intrinsic viscosity of maltose octanitrate fell upon the extrapolation of these curves; and that the nitrogen content of nitric esters of starches and dextrins was independent of degree of polymerization.

Experimental

Molecular Weight Determination.—One of us[4] who was familiar with a little known micro-isopiestic method of unusual simplicity,[5] proposed that it be tried for high polymers, a field in which the literature does not reveal a previous application of Barger's *specific techniques*, although Mark[6] states that variations of Barger's method have been used in the polymer field by certain European investigators.

Unfractionated solutions of nitric esters were prepared by weighing 0.5000 g. in a 100-ml. flask. Ethyl acetate was the standard solvent. Solutions of this concentration were used to prepare a series of solutions of concentrations ranging from 0.050 to 0.400 g./100 ml.

Solutions of known molecular weight were prepared from 1 *M* solutions of sucrose octaacetate[7] in ethyl acetate and diluting to various molarities.

For the determination a series of 7 drops was introduced in a capillary tube 6–7 cm. long with a bore of *ca.* 1 mm., in such a manner that a drop of the nitrate solution was interspersed between 2 drops of the acetate solutions. The first and the last drops, which were much larger than the other 5, were not measured. The remaining 5 drops, 3 of unknown nitrate and 2 of known acetate solutions, had an approximate length of 0.5 to 1 mm. and were separated by an air space of about the same thickness as the drops. The ends of the capillary tubes were closed with Plasticin which showed no marked attraction to the solvent. The tubes were mounted on 1 × 3-inch glass slides, with the help of straps of Plasticin, in order of increasing molarities, and kept in Petri dishes under a constant temperature of 25 ± 0.1°. The size of the drops was measured to 0.01 mm. A second reading was taken after eighteen to twenty-four hours, when complete equilibrium of the vapor pressure was reached.

The Barger method was cross-checked on an unfractionated polyvinyl acetate, the $\overline{M}_n$ of which, by osmometry, was reported as *ca.* 220,000. By the Barger method, a value of 240,000 was obtained on a sample of the same commercial type. Successive determinations on starch and dextrin nitric esters indicated a reproducibility within about 10%. The method is readily available to any laboratory and should have a wide application. In applying it, Barger's very detailed original work should be carefully studied, particularly in reference to probable sources of errors. It is particularly necessary to appreciate that it is the *direction* of the change in size of the drops, not the magnitude of the change, which is crucial.

Intrinsic Viscosity.—The unfractionated solutions in ethyl acetate which were used for molecular weight determinations, served also for determinations of $[\eta]$.

Viscosities were determined in calibrated Fenske tubes at 25 ± 0.1°. Specific viscosities were determined according to

$$\eta_{sp} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} - 1$$

Intrinsic viscosities were determined by extrapolation to zero concentration of the plot[8,9] of η_{sp}/c *vs.* c on semi-log paper.

Nitration of Starches and Dextrins.—All nitrations were run in accordance with the optimum conditions previously determined.[1]

Nitration of Maltose.—Ten grams of maltose monohydrate from Eastman Kodak Co. was dispersed in 150 ml. of chloroform and added under rapid agitation to 600 ml. of a chloroform solution of nitrogen pentoxide, of concentration 12.7 g./100 ml., in which 40 g. of sodium fluoride was dispersed. The nitration period was one hour, the initial temperature 2°, the minimum temperature −15°, and the maximum temperature at the close of the nitration period 7°. The product was filtered, washed and stabilized according to the method elsewhere described for the nitra-

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[1] Caesar and Goldfrank, THIS JOURNAL, **68**, 372 (1946).

[2] Intrinsic viscosity $= [\eta] = \lim\limits_{c \to 0} \eta_{sp}/c$.

[3] Bartovics and Mark, THIS JOURNAL, **65**, 1901 (1943).

[4] N. S. Gruenhut.

[5] (a) Barger, *J. Chem. Soc.*, **85**, 286 (1904); (b) Glasstone, *Textbook of Physical Chemistry*, D. Van Nostrand Co., New York, N. Y., 1940, p. 623.

[6] Private communication.

[7] From Niacet Chem. Corp.: *M* (theoretical) 678; *M* (Barger) 666.

[8] A. M. Sookne and M. Harris, *Ind. Eng. Chem.*, **37**, 475 (1945)

[9] Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351 (1944).

tion of starches.[1] The nitrogen value was 15.50%. If it be assumed that the water in maltose monohydrate reacts with nitrogen pentoxide to form nitric acid, which is taken up by the sodium fluoride, the theoretical value for nitrogen in the anhydrous octaester would be 15.95%, and the calculated molecular weight 680 at 15.50% *N*. The experimentally determined intrinsic viscosity was 0.016 (Fig. 3).

Nitration of Cellulose.—The procedure for the nitration of cellulose was the same as for starches and dextrins, except that the nitration time was longer (one hour).

Experimental Results and Discussion

Table I.—Illustrative of a molecular weight determination. It will be noted that the change in size of drops is in a constant direction up to a known molarity of 4×10^{-5}, *i.e.*, the knowns decrease in size and the unknowns increase; but that at 5×10^{-5}, a direction change has occurred: the drops of unknown have decreased and the known, increased. The isopiestic condition therefore lies between known solution molarities of 4×10^{-5} and 5×10^{-5}.

TABLE I

MOLECULAR WEIGHT DETERMINATION (APPARENT) BY BARGER METHOD. CORN STARCH TRINITRATE IN ETHYL ACETATE (4 g./l.)

Molarity (*m*) of known[a]	Change in drop measurements Unknown[b]	Known[a]	Unknown[b]	Known[a]	Unknown[b]
3×10^{-5}	+4	−2	+2	−3	+5
4×10^{-5}	+3	−3	+2	−4	+6
5×10^{-5}	−4	+3	−5	+4	−4

$\overline{M}_n$ (apparent) $= W/m = 4/4 \times 10^{-5} + 4/5 \times 10^{-5}/2 = 90{,}000.$

[a] Sucrose octaacetate. [b] Starch trinitrate.

TABLE II

NITRIC ESTERS OF CORN STARCHES, CORN PYRO-DEXTRINS AND MALTOSE: ETHYL ACETATE SOLUTIONS

No.	$\overline{M}_n$	[η]	% N	$\overline{DP}_n$
		Starches		
1[a]	74,000	0.74	13.91	252
2[b]	54,000	.50	13.95	184
3[b]	40,000	.31	14.03	135
4[c]	31,000	.34	13.74	107
5[d]	5,600	.078	13.99	19
6[d]	2,000	.047	13.92	6.8
7[dd]	2,200	.052	13.93	7.5
		Pyro-dextrins		
8[e]	2,000	.080	14.01	6.8
9[e]	1,700	.062	13.87	5.8
10[e]	1,500	.047	13.77	5.1
11[e]	1,000	.030	13.90	3.4
12[f]	1,300	.102	13.76	...
13[f]	1,000	.086	13.57	...
14[f]	1,000	.046	13.62	...
15[f]	900	.032	13.53	...
		Maltose		
16	680[g]	.016	15.50	2

[a] Commerical heavy-boiling starch. [b] Commerical thin-boiling starch. [c] Commercial chlorinated starch. [d] Special thin-boiling starch, twenty minutes nitration. [dd] Same, one hour nitration. [e] Commercial pyro-dextrin. [f] Special pyro-dextrin. [g] Calculated.

Table II.—Experimental results are summarized on nitric esters of commercial corn starches and dextrins, laboratory-prepared thin-boiling corn starches, and maltose. Experiments nos. 1–7 involve aqueous-processed starches; nos. 8–15 involve dry-processed starches in which heat is a principal reactant.

Two results are outstanding: (a) values of [η] for pyrodextrin nitrates are definitely higher, in respect to $\overline{M}_n$, than for the aqueous-processed starch nitrates; (b) nitrogen values are independent of $\overline{DP}$, approximating the triester value of 14.14%. The slightly lower than average nitrogen value for no. 4 is attributed to slight hypochlorite oxidation suffered by the starting material, and for no. 10 to non-carbohydrate impurities introduced in the manufacture of this dextrin. The possible structural significance of the relatively low nitrogen values of nos. 12–15, incl., will be subsequently discussed. The starting materials for this series represent a new and special type of conversion in which heat plays a greater role than in nos. 8–11, incl. The structural uncertainties implied by the abnormal nitrogen contents in nos. 12–15 preclude accurate calculations of $\overline{DP}_n$ from the observed $\overline{M}_n$ values.

Table III.—Molecular weights and intrinsic viscosities of trinitrates of cellulose, and of potato and corn amyloses, were determined for purposes of comparison. Owing to the small amount available of the potato amylose, the nitrogen content of its ester was not determined. The period of nitration (one hour) and the temperature range were such, however, as to make it reasonably certain that substantially complete esterification was attained.[1] The solubility in ethyl acetate of potato amylose nitrate was not quite complete, the soluble fraction being 93.2%. Its $\overline{M}_n$ and [η] are probably on the low side, considering the whole granule. Corn amylose nitrate is likewise incompletely soluble in ethyl acetate, but it was subsequently found that methyl acetate effected complete solution.

TABLE III

MISCELLANEOUS NITRIC ESTERS: CELLULOSE, POTATO, CORN. ETHYL ACETATE SOLUTIONS

$\overline{M}_n$	[η]	% N	$\overline{DP}_n$
	Cellulose[a]		
360,000	2.0	13.91	1230
	Potato amylose[b]		
290,000	0.84	...	980
	Corn amylose[c]		
64,000	.46	13.96	218

[a] Hercules Nitration Grade: degraded $(H_3O)^+$. [b] From Eastern Regional Research Laboratory. Soluble fraction 93.2%. [c] From Northern Regional Research Laboratory. Methyl acetate solution.

This problem of adequate solvation is obviously of paramount importance for $\overline{M}_n$ and [η] determinations. The higher the $\overline{DP}$ of whole starches the greater the difficulty of obtaining clear solutions of the undegraded nitric esters, even at very low concentrations. We have as yet been unable to obtain clear solutions of the trinitrates of unmodified whole potato starch and potato amylopectin, produced by nitrogen pentoxide nitration. Solution difficulties have been encountered, though to a lesser degree, with potato and corn amyloses (as previously noted) and occasionally with the triesters of whole corn starches. The problem appears to be related to branching of the polymers, not only in degree but in kind. In this connection it is interesting to note that the trinitrate of the cellulose sample (Table III) is readily soluble notwithstanding its relatively high $\overline{DP}_n$ of *ca.* 1,200, as compared to starches. The unfractionated nitric ester of the sample of potato amylose is less readily soluble than the cellulose ester, a result which probably arises from the presence of a little amylopectin component. Homogeneity in starches is exceptionally difficult to obtain, not only in respect to the unbranched and branched components but in clean-cut fractionation of polymer molecules. This is likewise true, though probably to a lesser degree, for cellulose nitric esters[10] and other polymers.[11] For these reasons it was felt that at this stage of the investigation of starch nitrates, it was advisible to work with *unfractionated* material. There is also the practical consideration that starch and cellulose are natural products in which polymer heterogeneity is inherent and not controllable to the extent of a synthetic polymer. It seems probable that for such reasons Gralen's extensive work on cellulose[12] was confined to unfractionated materials.

Figs. 1–3.—Graphical derivations, $c \rightarrow 0$, of $\overline{M}_n$ (Figs. 1–2), and of $[\eta]$ (Fig. 3), are shown for samples of nitric esters representative of the five principal types of starches investigated, *viz.*, commercial heavy and thin-boiling (expts. nos. 1 and 3), special very thin-boiling starch (no. 6), commercial hyrodextrins (no. 8), and special pyro-dextrins (no. 12). In addition, because of its interest and importance, the derivation of $[\eta]$ of maltose octanitrate is shown (no. 16) in Fig. 3.

The slopes of the curves in Figs. 1–3 are interesting and in the case of the $\overline{M}_n$ determinations of Figs. 1–2, difficult to rationalize. An unexpectedly high positive slope of the plot of $\overline{M}_n$ *vs.* c seems to be characteristic of the Barger method, although in some instances the slope is considerably reduced. Work now in progress on the nitric esters of Schardinger dextrins and sugars may shed some light on this point.

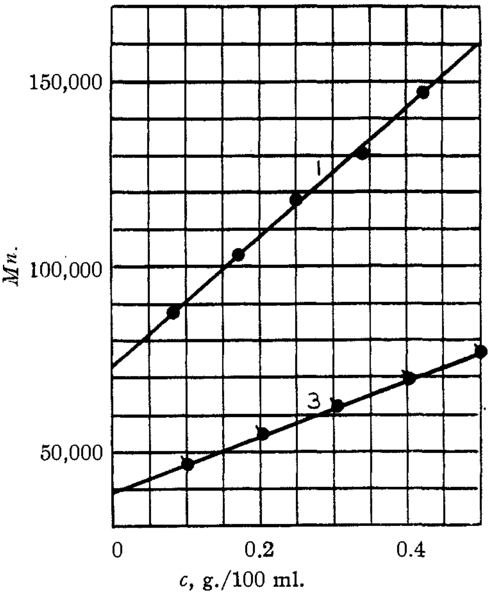

Fig. 1.—Derivation of $\overline{M}n$, nitric esters of commercial corn starches: 1 "heavy-boiling"; 3 "thin-boiling."

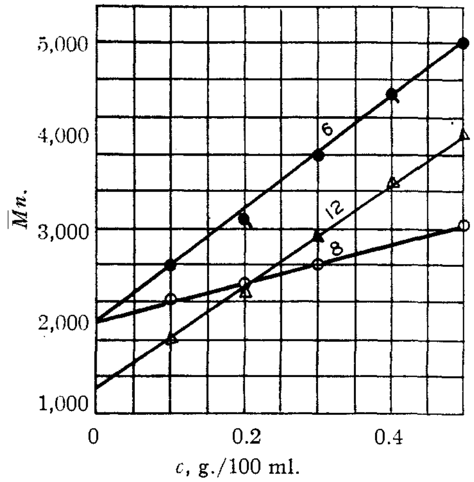

Fig. 2.—Derivation of $\overline{M}n$, nitric esters of modified corn starches: 6 special "thin-boiling"; 8 commercial pyro-dextrin; 12 special pyro-dextrin.

In Fig. 3, the nitric esters of the extremely thin-boiling starch (no. 6) and the heaviest of the commercial dextrin series (No. 8) have approximately the same $\overline{M}_n$, *ca.* 2,000 and $\overline{DP}_n$, 6.8, but their intrinsic viscosities are, respectively, 0.047 and 0.08, and the slopes of the plot of log η_{sp}/c *vs.* c, reversed. The plots of nos. 1, 3 and 8 show a decreasing value, with increasing concentration, of the ratio η_{sp}/c, an unusual result which appears to be typical of the nitric esters of these types of corn starch. The plot of no. 6 exhibits the normal positive slope, reported by other investigators of high polymers,[8,9] in which the ratio η_{sp}/c. increases with concentration. For the special pyro-corn dextrin (no. 12), the ratio ap-

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(10) Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

(11) Flory, THIS JOURNAL, **65**, 378 (1943).

(12) (a) Gralen, Dissertation, Upsala (1944); (b) Badgley, Frillette and Mark *Ind. Eng. Chem.*, **37**, 229 (1945).

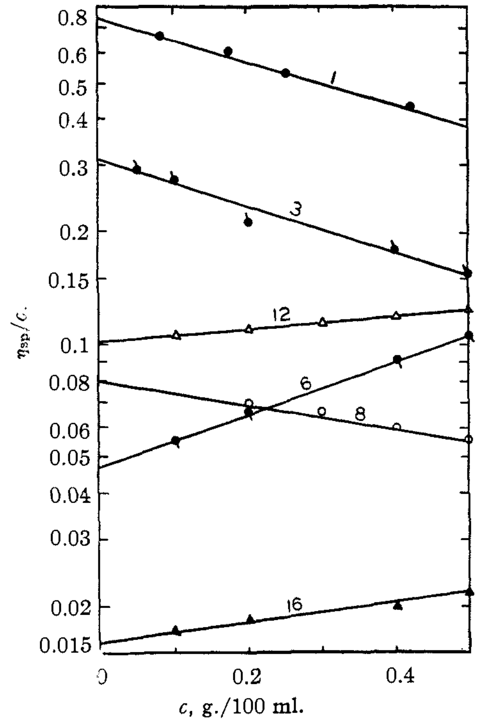

Fig. 3.—Derivation of $[\eta] = \lim_{c \to 0} \eta_{sp}/c$ vs. c—nitric esters: 1 "heavy-boiling" corn starch; 3 "thin-boiling" corn starch; 6 special "thin-boiling" corn starch; 8 corn pyro-dextrin; 12 special corn pyro-dextrin; 16 maltose.

proaches a constant, and the intrinsic viscosity, 0.102, is relatively high. According to a recent contribution on the enzymic synthesis of starch[13] such relative independence of concentration is significant of branching. It might also be significant of a rigid polymer molecule. This subject will be further discussed under Figs. 4–5.

Figs. 4–5.—In recent years an increasing number of investigations of high polymer solvent systems[3,8,11,12,14–18] is lending support to the simple relationship

$$[\eta] = KM^{a} \text{ (or } K\overline{DP}^{a}\text{)}$$

It is obvious that if this equation holds, the plot of log $[\eta]$ *vs.* log M (or $\overline{DP}$) is linear.

In Fig. 4 a classification into three linear plots log M *vs.* log $[\eta]$, is indicated from the experimental results. Curve A represents the nitric esters of corn *starches*, heavy to thin-boiling; B represents common "canary" or *pyro-dextrins*[3] C a special type of "*British gum*" pyro-dextrin.

Figure 5 represents plots of $\overline{DP}_n$ for A and B, and includes the data of Table III.

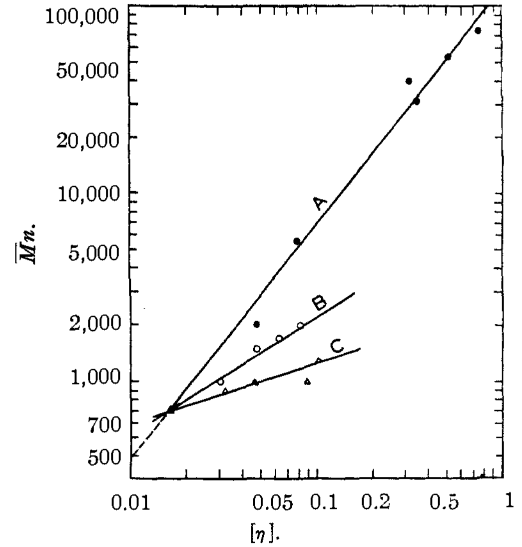

Fig. 4.—Relation of $\overline{Mn}$ and $[\eta]$: A corn starch nitric esters; B corn pyro-dextrin esters; C special corn pyro-dextrin esters; ▲ maltose octanitrate.

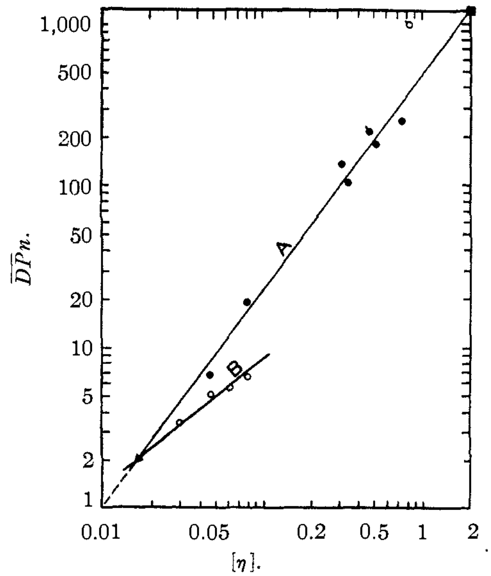

Fig. 5.—Relation of $\overline{DPn}$ and $[\eta]$: nitric esters, A corn starches ●, corn amylose ●, cellulose (degraded) ■; B corn pyro-dextrins O; potato amylose ọ; ▲ maltose.

One of the most interesting results of these plottings is that the experimental value for $[\eta]$ of maltose octanitrate falls on the curves for starches and dextrins. If this common intersection at the maltose unit structure be a mere coincidence, it is certainly a most remarkable one. Scarcely less interesting is the extrapolation of A to approximately the molecular weight of glucose pentanitrate, 405 (Fig. 4), and $\overline{DP}$ 1 (Fig. 5).

The experimental data, with the exception of the values for potato amylose, approximate a linear plot (Fig. 5) between maltose $\overline{DP}$ 2, and

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(13) Bourne and Peat, *J. Chem. Soc.*, 877–882 (1945).

(14) Coppick, *Paper Trade J.*, Aug. (1943).

(15) Kern and Fernow, *J. prakt. Chem.*, **160**, 307 (1943).

(16) Kern and Kaemerer, *ibid.*, **161**, 100 (1942).

(17) Alfrey, Bartovics and Mark, THIS JOURNAL, **65**, 2319 (1943).

(18) Matthes, *J. prakt. Chem.*, **162**, 245 (1943).

cellulose $\overline{DP}_n$ 1,240, an unusual range.[19]

This result, it is admitted, may be coincidental. It was certainly not anticipated. Further data are obviously desirable, especially on cellulose.

The long curves, A, of Figs. 4 and 5 represent hydrolytic degradation in aqueous suspensions, a depolymerization in which the anhydro-glucose chain units are supposedly unaltered structurally. As previously mentioned, the observed nitrogen contents are independent of $\overline{DP}_n$ and cannot be made to exceed an approximation to the theoretical value for the triester. This curious result would appear to suggest either a cyclic structure or the formation of an inner anhydride such as levo-glucosan, difficult to account for in aqueous acid degradations but already proven in the case of enzymic hydrolysis of waxy corn starch.[22] The fact is of considerable structural interest and merits further investigation.

The two short curves, B and C, of Fig. 4 represent *advanced* stages of dextrin conversions, the temperatures of conversion increasing from B to C. The increase in slope from curves A to C is tentatively attributed to heating and consequent dehydration[23] to form inner anhydrides such as levo-glucosan, a structural modification of anhydro-glucose chain units[24] which receives experimental support from the nitrogen contents of the dextrin nitric esters of Table II. Nitrogen content would be independent of $\overline{DP}$ for dehydration 1–6 (glucosan type), the theoretical value being 14.14%. Additional dehydration of glycide type would be reflected in a noticeable decrease in nitrogen content at low *DP*s. The mean nitrogen value for the B series is 13.89%; for the C series 13.65%.

Periodic acid oxidations of the original unnitrated materials, according to the Jackson and Hudson technique,[25] showed that the rate and extent of oxidation of samples no. 1, 4, 8, 11, 12, 13, 14 and 15 (Table II) were identical, which indicates that at least there is no involvement of hydroxyls at carbon 2 or 3 in glycide anhydride formation.

It has previously been stated that curves B and C of Fig. 4 represent *advanced* stages of dextrin conversions by dry heating. The initial stages of dry processing represent an extremely heterogenous condition in which the material has the properties of a degraded starch (curve A) and a pyro-dextrin (curves B and C). Incomplete data indicate that the simple relation $[\eta] = KM^a$ does not hold for the experimental results in the initial stages of a dry conversion when the temperature of the material is rapidly increasing. Curves B and C of Fig. 4 represent conversion ranges in which the temperature is approximately constant and time is the principal variable, increasing from right to left. In B, and particularly in C, $[\eta]$ varies greatly for a relatively small variation in $\overline{M}_n$. In A, which presumably involves aqueous degradation only, a similar variation in $[\eta]$ is reflected by a very much greater change in $\overline{M}_n$. The slope of the curves, represented by the exponent a, increases from A to C. This may be due to an increasing tendency in dextrinization to form rigid little molecules.[26]

The adhesive strength of the higher molecular weight dextrins of series C is exceptional.

Figures 4 and 5 indicate that a graphical classification of starch products may be possible, a result which, if confirmed by further investigations, is of considerable interest both scientifically and commercially.

Further investigations to augment experimental data and to clarify, if possible, the structural background of the results, are under way in this laboratory.

Acknowledgment.—We wish to thank Miss F. T. Moroz and Mr. M. Goldfrank for the preparation of the nitric esters used in this investigation.

Summary

Intrinsic viscosities and number average molecular weights were determined in ethyl acetate solutions of unfractionated nitric triesters of corn starches and corn dextrins. Molecular weights were determined by a new application of a simple micro-isopiestic method. Three types of starch conversions were explored: one wet-processing and two dry-processing. The experimental results appeared to satisfy Mark's variation of Staudinger's formula over an unusually wide range of degree of polymerization from wet-processed starches, and yielded three linear plots of log $\overline{M}_n$ *vs.* log $[\eta]$ with a common intersection at the experimental $[\eta]$ of maltose octanitrate. The possibility of a graphical classification of starch products was indicated. Dry-processed soluble dextrins were found to have a $\overline{DP}_n$ of <7. The nitrogen content of starch and dextrin esters could not be made to exceed the triester value. An apparently more rigid polymer molecule is indicated for pyro-dextrins than for starches.

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(19) Investigators of high polymer solvent systems, other than starch, have stated[3,20,21] that the simple relation $[\eta] = KM^a$ (or $\overline{DP}^a$) fails to satisfy the experimental results in very high and low ranges of $\overline{M}$ (or $\overline{DP}$). This rather widely held conclusion does not appear to apply, however, not only for the corn starch nitric esters studied in this Laboratory but for the extensive data on unfractionated cuprammonium solutions of celluloses reported by Gralen[12] in which a linear relation is indicated in the molecular weight range *ca.* 6×10^4 to 3×10^6.

(20) Badgley, *Polymer Bull.*, **1**, 17 (1945).

(21) Spencer and Boyer, *cf. ibid.*, **6**, 129 (1945).

(22) Montgomery and Hilbert, THIS JOURNAL, **68**, 916 (1946).

(23) Brimhall, *Ind. Eng. Chem.*, **36**, 72 (1944).

(24) T. C. Taylor, unpublished notes, 1938.

(25) Jackson and Hudson, THIS JOURNAL, **59**, 2049 (1937).

(26) Doty, Zimm and Mark, *J. Chem. Phys.*, **13**, 5 (1945).