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Determination of Degree of Nitration of Nitrocellulose by Refractometry

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Synopsis

Nitrocellulose (NC) films, when dried on a rigid substrate, tend to be biaxial and thus exhibit two refractive indices. The absolute difference between these indices has been found to provide an accurate measure of the degree of nitration of NC. A film of NC is cast from a 1% solution in butyl acetate to provide a film about 0.5 mil thick. The dry film, when placed in an Abbé-3L refractometer, gives two white lines which go to extinction alternately upon rotation of a cap analyzer through the east–west (EW) and north–south (NS) directions. Refractive index measurements are made using the line visible in each direction of the analyzer. The absolute difference between the two indices is related to the degree of nitration through standard curves for various grades of NC. The standard deviation for the proposed method was found to be ±0.01% N.

INTRODUCTION

Recent work by the authors[1] showed it is possible to determine the degree of nitration of nitrocellulose by using dispersion staining. This technique relies on noting the color produced by the refraction of light at the interface between nitrocellulose (NC) films and an oil of known refractive index. Different colors were observed for NC samples having different degrees of nitration. Thus the refractive index of NC was measurably affected by the degree of nitration. Although the technique was shown to be as accurate as the Nitrometer method,[3] it was believed too subjective for routine use where many technicians would be required to run the test. Therefore, it was decided to measure the refractive index of NC films and attempt to relate these results to the degree of nitration.

Several methods were explored for measuring the refractive index of films, viz., transmittance, grazing incidence, and total reflectance. Of these techniques, transmittance was the most successful. Initially, various oils having higher refractive indices than the films were used between the films and refracting prism. This technique produced a large dispersion, and accurate measurements were not possible because of hazy lines. Best measurements were made on dry films with no contacting liquid.

With all films, dispersion was noted at the critical angle. When correction was made with the Amici prism, two predominate white lines generally were visible. Using a cap analyzer over the eyepiece, each line could be

extinguished or brought to a maximum intensity in either the east–west (EW) or north–south (NS) direction, indicating double refraction.[2] Refractive indices were measured on NC films of varying nitrogen content. Attempts to relate either index to degree of nitration showed only a gross correlation. However, it was noticed that the difference between the two refractive indices for films of a given degree of nitration was constant, and this difference varied linearly with per cent nitrogen within a single grade of NC. Thus, the difference in the two measurable refractive indices of NC films provides a good measure of the degree of nitration (per cent nitrogen) of NC. Separate calibration curves are required for various grades (range of per cent nitrogen) of nitrocellulose.

EXPERIMENTAL

Materials

Apparatus required is an Abbé-3L refractometer (or equivalent), eyepiece cap analyzer, and glass plate (microscope slide).

Reagents were ethyl alcohol (absolute), butyl acetate (reagent grade), and nitrocellulose standards (samples of known nitrogen content as determined by Nitrometer method).

Procedure

Preparation of Film. Approximately 0.5 g of nitrocellulose is weighed out, and the sample is wetted with about 1 ml of ethanol; 50 ml of butyl acetate is added with stirring. When all fibers have dissolved, a small portion of the NC lacquer is poured onto a glass plate. The film is allowed to dry for about 30–40 min at ambient temperature or for about 15 min in an

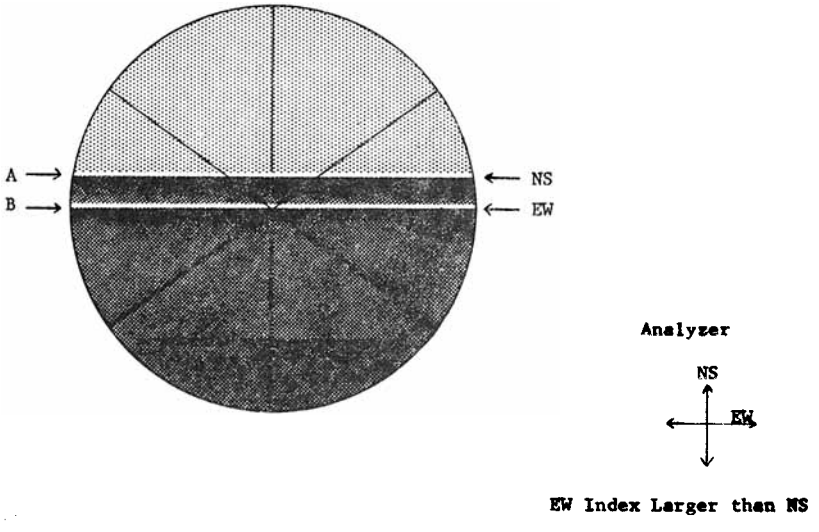

Fig. 1. Low-grade nitrocellulose film.

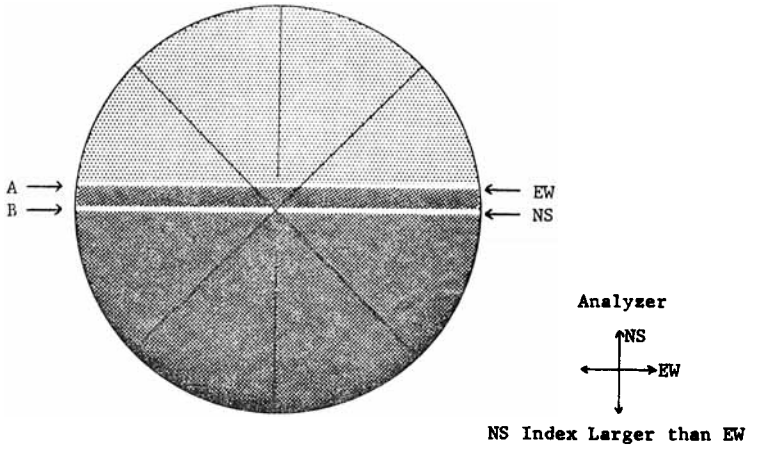

Fig. 2. High-grade nitrocellulose film.

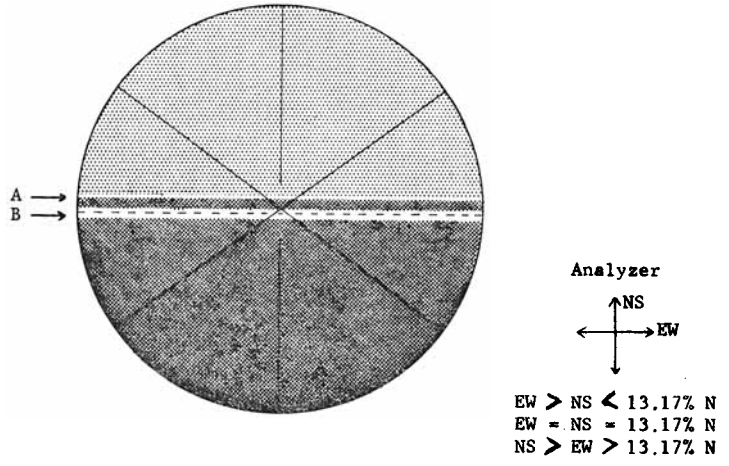

Fig. 3. Blends of high- and low-grade nitrocelluloses.

oven at 50°C. Care should be exercised in oven drying as the film may wrinkle badly if dried too fast. Such films cause high dispersion and are thus difficult to measure in the refractometer. After drying, the film is stripped from the glass. (Wetting with water aids in removing the film.) The film is dried with lint-free absorbent paper.

Refractive Index Measurements. The film is pressed onto the refracting prism to obtain good contact between the film and prism, and the refractometer is closed. The Amici prism and eyepiece are adjusted to give maximum sharpness of the two white lines used for measuring refractive indices of the films.

The cap analyzer is placed over the refractometer eyepiece and rotated; one line goes to extinction in the north–south (NS) orientation of the analyzer and the other in the east–west (EW) orientation. The refractive

index of the film at each orientation is then measured. For low-grade NC (12.6% N) the EW line will have the higher index (Fig. 1), while the reverse is true for the high-grade (13.4% N) NC (Fig. 2). The difference in the two refractive indices is obtained; reference to the appropriate curve yields the per cent nitrogen.

The lines used for measurement of high- and low-grade NC merge to a close doublet in blends of high and low grades, with a dark band appearing above the doublet. For some blends, the doublet is unresolved and appears as a single broad white line. The bottom of the doublet and the top of the dark band are measured (Fig. 3). The difference is obtained, and the per cent nitrogen can then be read from a standard curve.

Preparation of Standard Graphs. Prepare a standard graph for each grade of NC by using the procedure given above for preparation of films and refractive index (RI) measurements. ΔRI is plotted against per cent nitrogen as determined by the Nitrometer.

DISCUSSION

The proposed refractometric method has been used successfully for determining the degree of nitration of the two grades of fibers produced at this plant, viz., low-grade NC or pyronitrocellulose (12.6% N nominal), high-grade NC or gun cotton (13.4% N nominal), and blends of the two grades (13.1–13.3% N). Since the method is standardized against the Nitrometer, there is usually no bias between the methods. Results by both methods on typical production samples are given in Table I. Different results could be obtained by the two methods if a sample contained some fibers nitrated to such a low degree that they were insoluble in butyl acetate. In this case, the degree of nitration as determined by the refractometric method would be higher than that given by the Nitrometer. The refractometer result would represent the average degree of nitration of fibers that went into the cast film, i.e., those soluble in butyl acetate. The presence of fibers of low nitrogen ($<10.5\%$) in the grades of NC studied is rather uncommon. Therefore, this potential source of error is considered to be a very minor limitation of the refractometric method.

A study of the effect of temperature showed the absolute refractive indices to vary with temperature. However, the difference in the indices remained constant, showing the method to be insensitive to temperature at least over the range studied. These data are given in Table II.

NC films prepared as described in the procedure contain about 3–5% residual butyl acetate, which affects the measured refractive indices, i.e., as the residual solvent content in the films decreases, the refractive indices increase. Therefore, it would be necessary to have very close control on the drying of films for relating per cent nitrogen to either refractive index. Since both refractive indices change by the same amount with changes in residual solvent content, the difference in the two indices is independent of residual solvent content.

The precision of the refractometric method was calculated by using replicate results obtained on three samples of nitrocellulose of different nitrogen content. These data are given in Table III. The pooled standard deviation was found to be ±0.01% N. The standard deviation of the

TABLE I
Comparison of Nitrogen Contents by Refractometer and Nitrometer

NC grade	ΔRI × 10^{-4}	Nitrogen, %	
		Refractometer	Nitrometer
Low grade (12.6% N nominal)	15	12.69	12.71
	18	12.67	12.68
	21	12.65	12.65
	24	12.63	12.62
	24	12.63	12.65
	24	12.63	12.62
	26	12.62	12.62
	29	12.59	12.63
	30	12.58	12.58
	30	12.58	12.58
	32	12.57	12.55
	32	12.57	12.59
	33	12.56	12.57
	35	12.55	12.56
High grade (13.4% N nominal)	7	13.60	13.60
	10	13.53	13.49
	11	13.52	13.55
	11	13.52	13.53
	12	13.51	13.52
	12	13.51	13.51
	13	13.49	13.47
	13	13.49	13.52
	14	13.47	13.45
	14	13.47	13.49
	15	13.45	13.43
	17	13.42	13.42
	18	13.43	13.44
	21	13.36	13.36
Nitrocellulose blends (13.0–13.3% N)	7	13.25	13.25
	9	13.23	13.22
	10	13.22	13.17
	10	13.22	13.20
	15	13.18	13.17
	15	13.18	13.19
	16	13.17	13.17
	19	13.15	13.14
	20	13.14	13.10
	23	13.12	13.11
	25	13.11	13.12
	26	13.10	13.11
	30	13.07	13.09
	40	13.01	13.03

TABLE II
Effect of Temperature on Refractive Index Results

	NC grade	35°C	25°C	20°C
Refractive index readings	Low grade	1.5044EW	1.5050EW	1.5067EW
Refractive index readings	(12.63%	1.5020NS	1.5026NS	1.5044NS
$\Delta RI \times 10^{-4}$	N)[a]	24	24	24
Refractive index readings	High grade	1.5052NS	1.5059NS	1.5075NS
Refractive index readings	(13.47%	1.5039EW	1.5047EW	1.5062EW
$\Delta RI \times 10^{-4}$	N)[a]	13	12	13
Refractive index readings	Blend EW > NS (13.16% N)[a]	1.5032W	1.5032W	1.5048W
Refractive index readings		1.5015B	1.5015B	1.5030B
$\Delta RI \times 10^{-4}$		17	17	18

[a] Nitrometer result.

TABLE III
Precision Data[a]

	N, %		
	Low grade	High grade	Blend
	12.61	13.46	13.12
	12.61	13.46	13.11
	12.63	13.46	13.11
	12.63	13.47	13.14
	12.61	13.47	13.11
	12.61	13.46	13.12
Average	12.62	13.46	13.12

[a] $s_p = \pm 0.01\%$ N.

Nitrometer method in our laboratory was previously established to be $\pm 0.02\%$ N.

Film thickness was found to be a minor but easily controlled variable. Films having a thickness between 0.3 and 0.6 mil produce only one set of refraction lines. Films greater than about 0.6 mil produce multiple sets of lines. If lines from the same set are used, the results are unaffected. By using a 1% lacquer, films are produced that are about 0.5 mil thick and hence give only one set of lines.

Inadvertent stretching of films was considered as a possible source of error, as it could change the orientation of a film and possibly change one or both of the measured refractive indices. This was found not to occur, as films of the desired thickness tore before they could be stretched sufficiently to affect the results.

Small amounts of water in the NC do not interfere with film preparation or refractive index measurements. Therefore, undried NC can be used for analysis.

The time required for sample preparation and measurement in the refractometric method is less than 1 hr, in contrast with the 3 hr required

for the Nitrometer. Actual working time per sample for the refractometric method is 10 min versus 30 min for the Nitrometer.

Two other grades of NC were briefly examined to determine if the refractometer method was applicable. These were lacquer-grade (11.0–12.0% N) and dynamite-grade (12.2% N). For lacquer-grade NC, removal of the films from the glass slide was more difficult than for other grades. Refractive index measurements were made, and it was found that a ΔRI versus per cent N plot was linear. Again the EW index was higher. An interesting feature of these films was their high dispersion, which made it necessary to reset the Amici prism to read the NS line after reading the EW line. The dispersion also increased with decreasing nitrogen. Also, it was possible to dry these films so that a single index could be used to determine per cent N. A plot of the EW index versus per cent N showed linearity, the EW index increasing with a decrease in nitrogen content.

Only one sample of dynamite-grade NC was available for study. Results on this sample indicate that an extrapolation of the pyronitrocellulose calibration curve can be used for this grade. The lower limit of extrapolation is uncertain at this time.

Blends of lacquer-grade NC and pyronitrocellulose were prepared to give additional samples in the 12.0–12.5% N range. However, as with blends in the 13.15% N range, these blends were not the same as unblended nitrocellulose of the same nitrogen content. Although a technique similar to that used for blends in the 13.15% N range was used for the 12.0–12.5% N range, blends in the lower range present an additional problem, since they contain optically positive (lacquer grade) and optically negative (pyronitrocellulose) crystals.

References

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