JOURNAL OF APPLIED POLYMER SCIENCE VOL. 12, PP. 131–135 (1968)

Microscopic Determination of Degree of Nitration of Nitrocellulose with Dispersion Staining

J. A. KOHLBECK and W. T. BOLLETER,
Radford Army Ammunition Plant, Hercules Incorporated, Radford, Virginia 24141

Synopsis

A microscopical method with dispersion staining has been developed for determining the degree of nitration of nitrocellulose (NC). In the method the per cent nitrogen in unknown samples is obtained by matching the colors of dispersed refracted light between an oil of known refractive index and films of the unknown and an NC standard. Agreement with standard Du Pont Nitrometer results were excellent. Color differences were detected as the nitrogen content of the NC ranged between 12.55 and 13.5% with central screening and the polarizer. The sensitivity was found to be increased by crossing the analyzer with the polarizer and observing the phase differences resolved in the analyzer.

INTRODUCTION

Dispersion staining techniques have been reported for the identification of a variety of crystalline solids and for refractive index measurements.[1,2] The technique is based on the difference between refractive index dispersions of particulate solids and of the liquid medium in which the solids are immersed. In the present work this technique has been used for determining the degree of nitration (reported as per cent nitrogen) of nitrocellulose (NC). Cast films, rather than individual fibers, were used, to ensure homogeneity of the samples to be analyzed.

McNally and Sheppard[3] reported that films of NC could be isotropic, uniaxial, or biaxial, depending on drying conditions. Brown et al.[2] reported that biaxial films gave rise to a number of colors when observed with central screening (the polarizer and analyzer removed). The films used in this study were assumed to be biaxial, since a variety of colors was observed.

A biaxial film could assume any of four general types of orientation. These would be the vibration directions presented in the biaxial indicatrix. A section displaying only the β direction would not be possible in our case, for we observe more than one color. Of the remaining three general orientations one was preferential. If this were not the case, the colors would not be likely to be reproducible for any given nitrogen content.

EXPERIMENTAL

The dispersion staining objective used in this study was purchased from Walter McCrone Associates, Chicago, Illinois. This 10-power objective was equipped with annular and central screening. The refractive-index oils were obtained from the R. P. Cargille Laboratories.

In applying the dispersion staining technique to films it was found that central screening offered the best results, because all axial rays were stopped, and only those rays refracted at the film edge entered the microscope objective. When the analyzer was crossed with the polarizer, the technique became more sensitive, and color changes could be observed more easily. The analyzer functions as it should by analyzing the phase difference produced on the refracting edges of the crystal–liquid interface.

Color Observations

Liquids in the refractive index range 1.52–1.54 were selected for these studies, because the refractive indices of the film were near these values. For nitrogen values between 12.55 and 13.2% an oil of 1.520 index was adequate. Above 13.2%, however, very little color could be produced. When an oil index of 1.536 was used, colors were again observable in the range of 13.2 to 13.5% nitrogen. In Table I the colors observed between 12.55 and 13.2% nitrogen with a 1.520-index oil are given. Table II shows the colors observed for 13.2 to 13.5% nitrogen with a 1.536-index oil. It was necessary to rotate the stage to observe all of the colors for the various nitrogen levels.

TABLE I
Colors of Nitrocellulose Films (12.55–13.2% Nitrogen) in 1.520 Cargille Oil

Nitrogen, %	Colors[a]
12.55	Mostly white to yellow white
12.60	Yellow
12.67	Yellow, slight amounts of green
12.72	Yellow, slight amounts of green, blue
12.87	Yellow, blue, some orange
13.12	Yellow, blue, some red and orange
13.2	Orange-yellow, blue-white

[a] Increasing nitrogen content results in increasing amounts of blue; yellow also deepens in color.

TABLE II
Colors of Nitrocellulose Films (13.2–13.5% Nitrogen) in 1.536 Cargille Oil

Nitrogen, %	Color
13.2	Yellow, blue
13.4	Orange, red, blue
13.5	Blue-white, very little orange or red

The color ranges observed were measured between 74 and 77°F., the normal laboratory room temperature. As expected, an increase or decrease of temperature produced changes in the colors observed. For example, when the temperature was decreased to 55°F., some blues were observed in the 12.6% films. Heating had the opposite effect, such that blue almost disappeared from the 13.12% standard. Cooling or heating could be used to advantage; however, a complete study of the effects was not made in this investigation, since it was easier to use an oil of different refractive index to obtain the same effect.

Since temperature does have an effect on the observed colors, it is recommended that all measurements be made at 75 ± 5°F.

Selection of Refractive Index Oil

As stated, two different oils were used, depending on nitrogen content. To determine which oil to use, the degree of nitration of the incoming fibers was first estimated. The fibers nitrated at this plant are of two types: low grade (12.55–12.65%) and high grade (13.4–13.5%). Blends of the two are used for making intermediate nitration grades. The fiber grades were easily classified by using oils with indices ranging from 1.520 to 1.550. The best results were obtained with an oil of 1.544 index. Under the same conditions as for films the high-grade fibers displayed white colors, and the low-grade fibers gave colors from blue to yellow to dark red, on rotation of the stage. Blends of these two were likewise easily distinguished, since both types of fiber could be seen.

The degree of nitration of individual fibers may be determined by dispersion staining, since they produce the same colors reported in Tables I and II for films. The degree of nitration of individual fibers within a grade being variable, results from fibers are not a good measure of the average degree of nitration of a lot of NC; hence, the use of films to obtain a more representative sample. However, measurements of fibers could provide information on the range of nitration of fibers in a given lot.

Preparation of Films

Films were prepared by placing a few drops of a 1% NC lacquer in ethyl or butyl acetate on a microscope slide and allowing the solvent to evaporate. Acetone could not be used, because films cast from it were somewhat opaque. Other solvents were not tried.

When dry, the film was loosened from the slide with a razor blade and cut in small segments. The appropriate oil was then used for color observation and nitrogen determination. This technique gave reproducible films, as evidence from color observations. In some instances certain sections of a particular film did show variations from the general portion of the film. This did not occur frequently and appeared to cause no appreciable error.

Another variable considered was film thickness. It was shown that film thickness did not contribute to color variations. No rays passing

through the film were used, and purposely wrinkling or folding the film actually enhanced the amount of color by giving more edges at which dispersion could occur. This did not change the observed colors.

RESULTS

To obtain a measure of the precision and accuracy of the microscopic method, regular production samples were taken for analysis and the results compared with Nitrometer data (Standard Du Pont Nitrometer).[4] Results of this study are given in Table III. The standard deviation of

TABLE III
Microscopical vs. Nitrometer Method: Results

Sample	Type	Microscope N (observer no.), % 1	2	3	Avg.	Nitrometer N, %	Difference
1	Low-grade	12.60	12.60	12.60	12.60	12.60	0
2	Low-grade	12.55	12.60	12.55	12.57	12.58	−0.01
3	Blend	13.12	13.12	13.15	13.13	13.17	−0.04
4	Low-grade	12.60	12.60	12.55	12.58	12.55	+0.03
5	Low-grade	12.55	12.58	12.60	12.58	12.59	−0.01
6	Low-grade	12.60	12.60	12.60	12.60	12.59	+0.01
7	Low-grade	12.58	12.60	12.60	12.59	12.59	0
8	High-grade	13.47	13.50	13.45	13.47	13.43	+0.04
9	Blend	13.15	13.12	13.12	13.13	13.16	−0.03

the Nitrometer had been previously established in this laboratory to be ±0.02% nitrogen; the standard deviation of the microscopic method was found also to be ±0.02% nitrogen. The average difference in results between the two methods was ±0.02% nitrogen with a maximum difference of 0.04%.

References

1. K. M. Brown and W. C. McCrone, *Microscope Crystal Front*, **13**, No. 11 (1963).
2. K. M. Brown, W. C. McCrone, R. Kuhn, and L. Forlini, *Microscope Crystal Front*, **14**, No. 2 (1963).
3. J. G. McNally and S. E. Sheppard, *J. Phys. Chem.*, **34**, 165 (1930).
4. *Nitrocellulose*, MIL-N-244A, Feb. 13, 1962.

Résumé

Une méthode microscopique utilisant la coloration de la lumière dispersée a été développée en vue de déterminer la nitration de la nitrocellulose (NC). Dans cette méthode le pourcent en azote des échantillons non-connus est obtenu en comparant les couleurs de la lumière réfractée dispersée entre une huile d'indice de réfraction connu et les films de l'échantillon inconnu et d'un étalon NC. Les résultats sont en bon accord avec ceux fournit par le nitromètre standard DuPont. Une différence de couleur a été détectée lorsque la teneur en azote du NC se situait entre 12.55 et 13.5% en utilisant un écran central et un polariseur. La sensibilité augmente en croisant l'analyseur avec le polariseur et en observant les différences de phases résolues dans l'analyseur.

Zusammenfassung

Eine mikroskopische Methode mit Dispersionsanfärbung wurde entwickelt, um den Nitrierungsgrad von Nitrocellulose (NC) zu bestimmen. Bei dieser Methode erhält man den Prozentsatz an Stickstoff in unbekannten Porben dadurch, dass die Farben des gebrochenen Dispersionslichts zwischen einem Öl von bekanntem Brechungsindex und Filmen der unbekannten Probe und dem NC-Standard auf einander abgestimmt werden. Die Übereinstimmung mit den Ergebnissen des DuPont-Standard-Nitrometers war ausgezeichnet. Mittels einer Zentralblende und eines Polarisators wurden Farbdifferenzen festgestellt, wenn der Stickstoffgehalt der NC zwischen 12,55 Prozent und 13,5 Prozent lag. Die Empfindlichkeit nahm bei Verwendung gekreuzter Polarisatoren und Beobachtung der im Analysator aufgelösten Phasendifferenzen zu.

Received June 2, 1967
Prod. No. 1676