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Polarization Colors of Nitrocellulose

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Synopsis

The polarization colors of nitrocellulose (NC) fibers show an orderly progression from gray-white at 11.0% nitrogen (N) through first-order whites, yellows, and reds to second-order blue at 12.6% N. At higher levels of nitration, the polarization colors revert back to first orders with fibers containing 13.1% N showing gray changing to intense white at 13.5% N. The length-positive and length-negative character of NC fibers also changes with the degree of nitration. Fibers nitrated to about 12.4% N are optically neutral and become increasingly positive with a decrease in the level of nitration and increasingly negative as the level of nitration increases. This optical property and the polarization colors of NC provide much information about the level and range of nitration of NC fibers.

INTRODUCTION

Previous workers[1-6] reporting on the behavior of nitrocellulose fibers and gels in polarized light showed a relationship between the degree of nitration of NC and polarization colors. However, there was no general agreement in their findings, because of differences in sample preparation. Many solids and liquids have the ability to enter NC fibers and cause changes in polarization colors, either by stretching or swelling, which could account for much of the disagreement as few inert dispersion media were available to the early investigators. In the present work, Cargille oils were found to be inert to NC and were used as dispersion media. By using these oils, the polarization colors for NC, as reported in this paper, were found to be reproducible and directly correlatable to the degree of nitration regardless of the method of manufacture of the NC or the source of cellulose. The lighting was a 3200°K tungsten source. A tiffin 80A series filter can be used to eliminate much of the yellow from the tungsten source for photographing with high-speed Ektachrome. Other light sources such as a halogen or xenon could also be used as the colors observed are interference colors following the Neutonian color series.

The degree of nitration of NC is expressed as per cent nitrogen, and cellulose is commonly nitrated to contain from 11.0% to 13.5% N, depending on the end use of the NC. Lacquer-grade NC normally contains from about 11% to 12% N, while nitration levels (grades) above 12% N are of importance for military use. The level of nitration for a specific application may be achieved by nitrating all fibers to as close to the desired level as possible or by blending

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fibers of higher and lower nitrogen content to achieve the desired average per cent nitrogen. The properties of NC of the same per cent nitrogen prepared by these two techniques are, of course, different.

The most commonly used technique for measuring the nitrogen content of any grade of NC is the du Pont Nitrometer.[7] Although accurate, this method determines only the average nitrogen content of a sample and provides no information on the range of nitrogen content of the fibers making up the sample.

The authors previously reported on the determination of the degree of nitration of NC by dispersion staining[8] and refractometry.[9] These techniques also measure the average per cent nitrogen, but some information is obtained about the range of nitrogen content by the dispersion staining technique, and the refractometer can be used to distinguish certain NC blends from NC uniformly nitrated to the same level. At times, it is important to know the nitration range for NC from a single nitration and the approximate nitrogen content of fibers in a blend. Observation of individual fibers under polarized light, as described in the present paper, has been found to be the most satisfactory method for obtaining this information.

EXPERIMENTAL

Place a small amount of dried NC fibers on a microscope slide and add a drop of a Cargille liquid having a refractive index between 1.51 and 1.53. Other liquids in this refractive index range may be used so long as they do not swell or stretch the NC fibers. Mix the fibers and the oil with a small spatula and cover with a No. 1 cover slip. Place the slide on a mechanical microscope stage and scan, using crossed polarized light. Rotate the stage and observe the polarization colors of the fibers. To determine the length negative or length positive nature of NC fibers, insert a first-order gypsum plate, rotate the mechanical stage, and note the vibration directions of the slow and fast rays of the gypsum plate with respect to the length and width of the fibers. If the fast ray direction of the gypsum plate is parallel to the long axis of the fiber, a first-order yellow will be observed for a length positive fiber while a second-order blue will be observed for a length negative fiber (i.e., the ray vibrating parallel to the long axis is slower or faster than the ray vibrating at right angles to the long axis). Of course, with higher-order colors, the effect of the gypsum plate on the order would change accordingly. With NC fibers, however, polarization colors do not exceed second order blue.

DISCUSSION

Nitrocellulose fibers follow the uniform progression of polarization colors described by Michel-Levy[10] from first-order gray-white at 11.0% N to second-order blue at 12.6% N. The colors for NC fibers in this range as well as for higher degrees of nitration are shown in Table I.

Another important optical property of NC is observed in the nitration range between 12.0% and 12.6% N. This property is the change from length positive to length negative and occurs at approximately 12.4% N. Fibers nitrated to 12.4% N show a first-order red and remain so with a gypsum first-

TABLE I

Polarization color	Order	% N	
Gray white	1st	11.0	Increasingly length positive
White	1st	11.5	
Yellow white	1st	11.7	
Yellow	1st	12.0	
Orange	1st	12.2	
Red orange	1st	12.3	
Red	1st	12.4	Optically neutral
Violet	2nd	12.5	Increasingly length negative
Blue	2nd	12.6	
Blue white	2nd	12.8	
Pale gray	1st	13.1	
Gray	1st	13.2	
White	1st	13.4	
Intense white	1st	13.5	

order accessory plate regardless of orientation (i.e., the fibers are optically neutral). Below 12.4% N, the fibers become increasingly length positive with decreasing nitrogen content, while the reverse is true above 12.4% N. The intensity of the yellow color of fibers containing less than 12.4% N and the blue color of fibers nitrated above 12.4% N is greatest when the fast ray of the accessory plate is parallel to the long axis of the fibers. If an optical densitometer were used, the length fast or length slow nature of the fibers would be an accurate measure of nitrogen content of NC fibers.

Fibers nitrated to about 12.8% N are blue-white, with the blue character of the color decreasing as the level of nitration increases. If the normal progression of polarization colors were followed, a second-order green or red would be expected for fibers containing 13.15% N. However, the fibers nitrated to this level are first-order gray. Fibers nitrated to about 13.5% N show a first-order white, however, the intensity of the color is significantly greater than that observed for fibers containing 11.5% N. Very highly nitrated fibers (nitrogen content uncertain but greater than 13.6% N) show second-order green with a first-order gypsum plate.

Although the orderly progression of polarization colors does not continue for NC nitrated above 12.6% N, the negative optical orientation of fibers does continue in a uniform fashion.

The polarization colors for a given nitration level are the same whether the NC is made from wood pulp or cotton linters. However, the range of nitrogen content within and between fibers for any grade is usually different for the two types of NC. Nitrocellulose made from linters has a more uniform degree of nitration than NC made from pulp; e.g., for pyronitrocellulose (12.6% N) made at this plant, the range of nitration between fibers is ±0.4% N for linters and ±1.0% N for pulp. Many factors can, of course, affect this range.

By using the above information and a little practice, accurate estimates of the nitrogen content of NC can be made in less than 1 min. A large number of samples have been observed in this laboratory over the last several years and their nitrogen content estimated by the use of the polarizing microscope. These estimations were compared with the results from the nitrometer; they were always within 0.1% N of the nitrometer result, and the difference was usually less than 0.05%. In addition to a rapid, reasonably accurate estimate of the nitrogen content, a polarizing microscope offers the added advantage of providing vital information of the uniformity of nitrogen content and whether a particular sample is a blend or made up of fibers nitrated to a nominal level.

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