# PREPARATION OF LOW VISCOSITY CELLULOSE NITRATE

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**Abstract.** Low viscosity cellulose nitrate is generally prepared by carrying out degradation of nitrated cellulose with steam under high pressure. In the present investigation this hazardous step was avoided by first degrading cellulose with hydrochloric acid under controlled conditions and then nitrating it. Cellulose nitrate prepared in this way was comparable with the imported material.

Low viscosity cellulose nitrate is mainly used in protective and decorative coatings. Cellulose nitrate, having intrinsic viscosities in the range of 0.4 to 5 corresponding to a degree of polymerisation of 70–850 anhydroglucose unit per molecule is used for this purpose. Commercially the viscosity of cellulose nitrate is expressed in other units such as seconds or centipoises. Most commonly used viscosities are $\frac{1}{2}$ and $\frac{1}{4}$ seconds.

Low viscosity cellulose nitrate is not being manufactured in Pakistan though raw material, i.e. cotton linters, nitric acid and sulphuric acid is available in abundance. Cellulose nitrate worth more than Rs. 1.45 lac was imported in Pakistan during July 1969 to June 1970 by the paint industry. With the availability of the material within the country, its use is bound to increase.

The viscosity of cellulose nitrate in solution depends upon its degree of polymerisation and its nitrogen content. The nitrogen content of cellulose nitrate meant for lacquers is about 12%. Nitrogen content has not got such a marked effect on its viscosity as the degree of polymerisation that determines the viscosity of a given sample of cellulose nitrate. A number of methods have been prescribed in the literature for reducing the viscosity of cellulose nitrate. It can be reduced by aging the solution.[2] This method has the only advantage that no loss of nitrogen occurs. On the other hand, it is highly time-consuming and inefficient process. Treatments with ammonia, sodium hydroxide, solution of ammonium nitrate and hydrochloric acid vapours had also been prescribed.[3] All these methods were of theoretical interest. On commercial scale low viscosity cellulose nitrate is prepared by digesting slurry of nitrated cotton in water with steam at high pressure.[4] Removal of gases, generated due to the denitration of cellulose nitrate creates difficulties. The gases may even cause explosion. Therefore, such an operation is carried out in heavily barricaded vessels. Some of the difficulties of this method were overcome by carrying out the reaction in continuous digesters.[5] In the continuous process, cellulose nitrate suspended in water is pumped through a special alloy tubular reactor. This reactor is about 4,000 ft long and is heated to various degrees. The temperature and time of residence determines the viscosity of cellulose nitrate. The continuous process is suited only to high rate of production and it requires expensive equipment. To overcome these difficulties a simpler process was devised in which degree of polymerisation of cellulose was first reduced and then it was nitrated.

Nitric acid alone, in the form of liquid or vapours, can be used for nitration of cellulose. In the present investigation the traditional method, which employs a mixture of nitric acid and sulphuric acid, was used. Nitration involves the usual principle of esterification. Reaction starts immediately on mixing of the reactants. It attains an equilibrium condition after sometime. The degree of nitration is governed mainly by the composition of the nitrating mixture. Increase in the quantity of sulphuric acid results in higher degree of nitration through removal of water. The concentration and the temperature of the reactants had to be rigorously controlled for uniform results.

Stability of the product is as important as the degree of nitration. Unstable nitrocellulose will result in general embrittlement and disintegration of the film. Coatings will crack and peel off after sometime[6]. If not properly stabilised, the cellulose nitrate may even explode during storage.

The unstability of cellulose nitrate is attributed to the formation of cellulose sulphate during nitration. Various methods have been suggested for improving its stability such as washing readily decomposable cellulose sulphate or first hydrolysing the combined sulphate and then washing it by different methods. Beating of nitrated cotton linters in hollanders, treating them with aqueous ammonia,[7] squeezing them in hydraulic presses,[8] heating them in water above 100°C under pressure[9] and extracting them with alcohol under various conditions,[10] had been suggested in literature. In the present investigation nitrated cellulose was boiled with dilute sodium carbonate to stabilise it.

### Experimental

*Depolymerisation.* Cotton linters were digested with dilute alkali to remove wax and lignin. These were dried and used for depolymerisation. Usually 2.5 g dry alkali-treated cotton linters were taken in a beaker. Hydrochloric acid of various known concentrations was then added in the ratio 40 ml acid to 1 g cotton. The time of addition was noted and the beaker was allowed to stand for a specific period at room temperature or at higher temperature as the case may be. After expiry of the period the contents were

Table 1. Effect of HCl Treatment on Degree of Polymerisation and Viscosity of Cellulose Nitrate.

| HCl used for degradation | Tempera-ture of degradation | Time of degradation (min) | Nitrogen content | Intrinsic viscosity | Degree of polymeri-sation | Viscosity (sec) |
|---|---|---|---|---|---|---|
| HCl (concd) | 26°C | 20 | 12.02 | 4.30 | 1162 | 1000 |
| ,, | ,, | 40 | 12.18 | 2.65 | 716 | 100 |
| ,, | ,, | 90 | 12.38 | 1.55 | 419 | 7 |
| ,, | ,, | 120 | 12.35 | 0.85 | 230 | 0.7 |
| ,, | ,, | 150 | 12.36 | 0.71 | 191 | 0.3 |
| HCl (10%) . | B.p. | 10 | 12.34 | 0.97 | 262 | 1.1 |
| ,, | ,, | 20 | 12.38 | 0.75 | 200 | 0.4 |
| ,, | ,, | 30 | 12.40 | 0.59 | 159 | 0.2 |
| HCl (5%) | ,, | 5 | 12.19 | 2.65 | 716 | 100 |
| ,, | ,, | 15 | 12.27 | 1.75 | 473 | 12 |
| ,, | ,, | 27 | 12.34 | 0.99 | 268 | 1.5 |
| ,, | ,, | 35 | 12.35 | 0.89 | 241 | 0.75 |

transferred into a beaker full of water. Degraded linters were then washed thoroughly by decantation and dried in an oven.

*Nitration.*[11] The nitrating mixture was prepared by mixing 62.8 g $HNO_3$ (concd, 70%) with 7 g distilled water followed by careful addition of 113.5 g $H_2SO_4$(concd). Addition of $H_2SO_4$ caused an abrupt rise in the temperature of acid mixture, hence it was cooled down and maintained at 36°C with the help of a thermostat. This temperature was maintained during nitration.

Two grams acid-treated cotton linters were added to the nitration mixture which was occasionally stirred. After 25 min nitrated product was picked up from the acid mixture and transferred to a 2-litre beaker full of water. It was then thoroughly washed with water till completely free from acid.

*Stabilization.* The nitrated linter though free from acid still contained some $H_2SO_4$ and sulphate ions either in combined or an adsorbed state. Nitrated linters were, therefore, treated with $Na_2CO_3$ (1%) for 5 min, washed then boiled in water, and dried in hot air.

*Determination of Nitrogen Content.*[12] The nitrogen content was measured by Lunge's method. 0.1 g completely dried sample was covered with 6–8 ml $H_2SO_4$ (concd). It was allowed to stand till fibrous structure of nitrocellulose disappeared. The sample in $H_2SO_4$ was transferred to Lunge's reaction tube with the help of small quantity of $H_2SO_4$ and 0.5 ml water. The tube was shaken gently til! no more gas evolved. The correction for sulphuric acid column was applied in the usual way and nitrogen content calculated from the volumes of gas reduced to N.T.P.

*Degree of Polymerisation.* The degree of polymerisation was calculated from intrinsic viscosity. For this purpose nitrated linters were dissolved in acetone in five different concentrations ranging from 0.1 to 0.5 g/100 ml. Viscosities of these solutions and pure acetone were determined by Ostwald viscometer at 26°C. Intrinsic viscosities were determined by extrapolating curve of specific viscosity against concentration to zero concentration. Degree of polymerisation was calculated from the well-known Staudinger equation. $(\eta_{sp}/C)_{c=0} K_m P$.

where $P$ is degree of polymerisation and $K_m$ is a constant having a reported value $3.7 \times 10^{-3}$ for nitrated cellulose of about 12% nitrogen content.[13]

Some authors prefer to calculate degree of polymerisation by multiplying intrinsic viscosity with 170.[14] This will obviously give lower value of degree of polymerisation. Intrinsic viscosity is converted into seconds according to the monograph of Ott and Spurlin.[15]

## Results and Discussions

The experimental results are given in Table 1. By proper selection of such variables as concentration of HCl, temperature and time of treatment, cellulose nitrate of any desired viscosity can be obtained. Dilute acid at boiling temperature is preferable for reasons of material and time economy. 5% HCl is preferable to 10% HCl because degradation progresses at an intermediate rate and can be controlled easily. The cellulose nitrate of 1, $\frac{3}{4}$ and $\frac{1}{2}$ seconds viscosities commonly used by paint industry can be obtained by boiling linter in 5% HCl for 30, 35 and 40 min respectively before nitration. Alternately cotton linters can be boiled with 10% HCl for 10, 20 and 30 min to get cellulose nitrate of approximately 1, $\frac{1}{2}$ and $\frac{1}{4}$ seconds viscosity. This method is free from hazards of high temperature treatment of nitrated cellulose and allows full control of degree of polymerisation. The equipment required is simple and is equally suitable for batch or continuous operation.

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