

## 2.1.2. Cellulose Nitrate

Summary monographs on cellulose nitrate in addition to those in the Reference list can be found in [21] and [22].

### 2.1.2.1. Physical Properties

Cellulose nitrate (CN) is a white, odorless, and tasteless substance. Its characteristics are dependent on the degree of substitution.

### 2.1.2.2. Chemical Properties

The three hydroxyl groups of cellulose can be completely or partially esterified by nitrating acid. The varying degrees of nitration can be related to the following theoretical nitrogen contents:

Cellulose mononitrate,  $C_6H_7O_2(OH)_2(ONO_2)$ :

6.75 % N

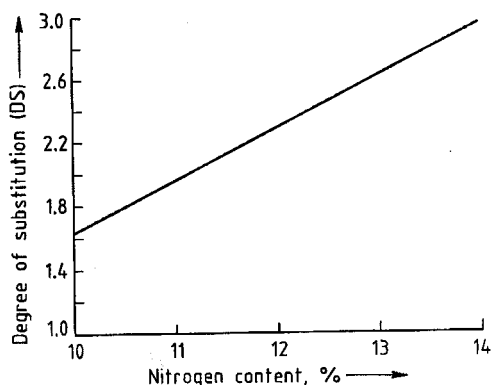
Cellulose dinitrate,  $C_6H_7O_2(OH)(ONO_2)_2$ :

11.11 % N

Cellulose trinitrate,  $C_6H_7O_2(ONO_2)_3$ : 14.14 % N

Cellulose nitrate with a nitrogen content between 10.8 and 12.6 % is a suitable raw material for lacquers, and CN with > 12.3 % N is suitable for explosives exclusively.

*Degree of Substitution – Nitrogen Content – Solubility.* The degree of substitution can be calculated from the nitrogen content of the various CN types (Fig. 1). The degree of substitution determines the solubility of cellulose nitrate in organic solvents. CN for lacquers can be classified according to its solubility in organic solvents as follows:



**Figure 1.** Variation of the degree of substitution with the nitrogen content of cellulose nitrate

alcohol-soluble CN (A types)

nitrogen content: approx. 10.9–11.3%

readily soluble in alcohols, esters, and ketones

moderately soluble CN (AM types)

nitrogen content: approx. 11.4–11.7%

soluble in esters, ketones, and glycol ethers with excellent blendability or compatibility with alcohol

CN soluble in esters (E types)

nitrogen content: 11.8–12.2% for lacquer cotton, up to 13.7% for guncotton

readily soluble in esters, ketones, and glycol ethers

*Intrinsic Viscosity – Degree of Polymerization* [24, pp. 85–121]. The mean number of anhydroglucose units in cellulose nitrate molecules is designated as the mean degree of polymerization (DP). The viscosity of the solution (at the same concentration in the same solvent) is generally considered to be a relative measure of the molecular mass. The molecular mass can be mathematically expressed as a function of the intrinsic viscosity (Staudinger–Mark–Houwink equation).

*Distribution of the Molecular Mass.* The starting material of cellulose nitrate is natural cellulose, the quality of which is subjected to annual growth cycles. It is, therefore, of great importance to have polymolecular data, such as the mean degree of polymerization and the distribution of the molecular mass, available in addition to viscosity, solubility behavior, and nitrogen values. These values are important, for example, in assessing the mechanical properties and aging processes of polymer products.

The isolation of the polymers according to their molecular mass can be achieved elegantly by gel permeation chromatography (GPC).

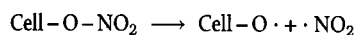
*Chemical Compatibility.* An every day use of cellulose nitrate is in nitro lacquers, where it is dissolved in organic solvents. In this solution, cellulose nitrate is extremely compatible with essential substances in the lacquer formulation such as alkyd resins, maleic resins, ketone resins, urea resins, and polyacrylates. A large number of softeners, such as adipates, phthalates, phosphates, and raw and saturated vegetable oils are compatible with cellulose nitrate.

*Chemical and Thermal Stability.* Cellulose nitrate, as a solid or in solution, should not be brought into contact with strong acids (degradation), bases (denitration), or organic amines (decomposition) since they all induce a destruction of cellulose nitrate. This may proceed very rapidly and lead to deflagration of the cellulose nitrate.

The ester bonds of cellulose nitrate, which can be broken by saponifying agents or by catalysis, are responsible for its physicochemical instability. This substance-specific property is dependent on the temperature, the specimen, and whether catalytically active decomposition products remain or are removed from the sample.

Another basic instability of cellulose nitrate is observed during the production process. Mixed sulfuric acid esters transmit a chemical instability to the nitrocellulose molecule. These mixed esters are destroyed in weakly acid water during the stabilization phase of production. The long reaction time required by this procedure can be considerably shortened by increasing the reaction temperature. The time required can be reduced to only a few hours by raising the temperature to 60–110 °C. Under these conditions the nitrate ester remains stable; the glucosidic bond of cellulose nitrate, on the other hand, is attacked. This property is used to advantage to specifically reduce the degree of polymerization of the cellulose nitrate.

Thermogravimetry, IR spectroscopy, and electron spectroscopy (ESCA) [26], [27] have recently been used to determine the extent of thermally induced and light-induced decomposition of cellulose nitrate. The reaction proceeds as follows:



It is preceded by a series of extremely exothermic oxidation reactions triggered by the  $\text{NO}_2$  radical, which often leads to spontaneous deflagration.  $\text{NO}_2$  is reduced to  $\text{NO}$  and in the presence of air  $\text{NO}_2$  is reformed, thus initiating an autocatalytic chain reaction, at the end of which the gaseous reaction products  $\text{CO}_x$ ,  $\text{NO}_x$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{HCHO}$  are found.

By adding stabilizers such as weak organic bases (diphenylamine) or acids (phosphoric acid, citric acid, or tartaric acid), intermediary nitric oxides can be bound and the autocatalytic decomposition prevented.

Thermal decomposition does not occur at temperatures below 100 °C. The temperature (according to [28]) at which cellulose nitrate spontaneously deflagrates is used as a measure of its thermal stability. A well-stabilized lacquer cotton has a deflagration temperature of  $\geq 180$  °C. The deflagration temperature of plasticized cellulose nitrate chips with at least 18 wt% softener (i.e., dibutyl or dioctyl phthalate) is  $\geq 170$  °C.

The Bergmann–Junk test [29] and the warm storage test are additional methods for determining the stability of cellulose nitrate.

## 2.1.2.5. Commercial Types and Grades

Cellulose nitrates receive, because of their fluffy structure and cottonlike appearance, the additional designation "cotton."

Two parameters are decisive for the industrial use of cellulose nitrate:

1519

**Table 6.** Cellulose nitrate types

Type	N content, %	Degree of substitution (DS)
Celluloid cotton	10.5–11.0	1.82–1.97
Alcohol-soluble lacquer cotton	10.9–11.3	1.94–2.06
Lacquer cotton moderately soluble in alcohol	11.4–11.7	2.08–2.17
Ester-soluble lacquer cotton	11.8–12.2	2.20–2.32
Powder cotton	12.3–12.9	2.55–2.57
Guncotton	13.0–13.6	2.58–2.76

Nitrogen content (including the resulting solubility properties)

Viscosity

As seen in Table 6, cellulose nitrates with differing nitrogen contents have various applications. Cellulose nitrates for lacquers are available in numerous viscosities. It is possible to categorize all stages of viscosity according to the European norm (DIN 53179), but the viscosity of cellulose nitrates is primarily categorized by using the Cochius method and the British or American ball drop method (ASTM D 1343-69).

In addition to the so-called cotton types densified CN types are available. These may be obtained by either nitrating compressed cellulose or by subsequently compressing the fluffy cellulose nitrate. It is possible to almost double the bulk density by compression.

For safety reasons, the commercially available CN cotton types must be wetted with at least 25 wt% water or aliphatic alcohols. In addition to water, ethanol, *n*-butanol, and 2-propanol may also be used as wetting agent.

The largest manufacturers of cellulose nitrates are the following:

Hercules Inc.	USA
Wolff Walsrode AG	FR Germany
Hagedorn	FR Germany
WNC Nitrochemie GmbH	FR Germany
Société Nationale des Poudres et Explosifs (SNPE)	France
Imperial Chemical Industries (ICI)	Great Britain
S.I.P.E. Nobel S.p.A.	Italy
Unión de Explosivos Río Tinto S.A.	Spain
Bofors	Sweden
Asahi	Japan
Daicel Chemical Industries, Ltd.	Japan

Many countries in South America, Asia, and Eastern Europe maintain small CN production facilities. The total world capacity may be estimated to 150000 t/a of dry cellulose nitrate.

### 2.1.2.7. Uses

**Explosives.** Explosives may be categorized according to their use:

- blasting agents
- propellants and shooting agents
- detonating agents
- igniting agents
- pyrotechnical agents

Cellulose nitrates are used primarily as propellants and gun powder, whereby the following distinctions can be made: *monobasic powder*, which is based solely on cellulose nitrate; *dibasic powder*, which contains further energy carriers such as, for example, nitroglycerin or diglycol dinitrate in addition to cellulose nitrate; *tribasic powder*, which contains in addition to the components of the dibasic powder a third agent such as nitroguanidine.

The selection of the cellulose nitrate is of special importance. The types of cellulose nitrates that differ in the degree of nitration were standardized as follows:

CP I	(Collodium powder) also known as guncotton, nitrogen content: 13.3–13.5 %
CP II	(Collodium) nitrogen content: 12.0– 12.7%, mostly 12.6 %
PE	(Powder standard) nitrogen content: 11.5–12.0%, mostly 11.5 %

Aromatic amines, such as diphenylamine, are added to gunpowder as stabilizers. They are capable of binding the nitrous gases generated during the decomposition of the nitric acid ester. A mixture of ca. 80 % highly nitrated gunpowder (13.4 % N) and ca. 20 % less-nitrated collodium cotton (12.5 % N) is used for the production of the monobasic propellant powder. Since cellulose nitrate granules are easy to charge electrostatically, they are made conductive with a fine graphite coating.

The multibasic powders usually contain cellulose nitrate CP II. Mixtures of 40 % PE cotton and 60 % CP I are also used because they have the same energy content as CP II with 12.6 % N.

The introduction of a third component to tribasic powder results in a lower heat of combustion in comparison to dibasic powder, thereby lengthening the life of the gun barrel.

Gunpowder is used in small-arms ammunition as well as large-caliber guns and tanks.

**Lacquers.** Cellulose nitrate lacquers are characterized by the outstanding film-forming properties of the physically drying cellulose nitrate. Moreover, cellulose nitrate is compatible with many other raw materials used in lacquers and can be used advantageously in combination with resins, softeners, pigments, and additives.

In addition to the nonvolatile lacquer components, the composition of the solvent mixture is decisive for the formation of a film.

The most important uses for nitro lacquers are as follows: wood lacquers (especially furniture lacquers), metal lacquers, paper lacquers, foil lacquers (also as hot sealing lacquers, e.g., cellophane, plastic, and metal foils), leather lacquers, adhesive cements, putties, and printing ink (for flexo and gravure printing).

The processes used for applying cellulose nitrate lacquers to substrates are as follows: spraying (compressed-air, airless, and electrostatic spraying), casting (for example, with a curtain coater), rolling (especially for the application of small amounts of lacquer), doctor knife coating, and dipping.

The casting and rolling processes are used for lacquering large, even areas. Irregularly shaped objects are sprayed. The choice of a suitable type of cellulose nitrate (e.g. completely or moderately soluble in alcohol, soluble in esters, degree of viscosity) is dependent on the lacquer type. A highly viscous cellulose nitrate type is used if elastic and thin applications are desired (e.g., leather). However, if hard and thick layers are desired, low-viscosity types are preferred.

**Table 8.** CN lacquer cottons

Ester-soluble type	Alcohol-soluble type
Possible use of alcohol in the lacquer formulation	Use of alcohol, especially ethanol, in any desired amount as a solvent
Good dilutability with aliphatic and aromatic hydrocarbons	Good dilutability with aromatic hydrocarbons
Very rapid solvent release	Rapid solvent release
Formation of hard films	Formation of films with thermoplastic properties
Attainment of good mechanical properties as far as the cold-check test, stretch, hardness, and tensile strength are concerned	Attainment of good mechanical properties; some special problems of lacquer production may be solved such as:  Lacquers which can be diluted with ethanol in any desired manner (wood polishes) Odorless lacquers (printing inks) Gel dipping lacquers Hot sealing waxes (cellophane lacquers and aluminum foil lacquers)

The concentration or the degree of viscosity of the cellulose nitrate determine the viscosity of the lacquer solution. However, the formulation of the lacquer must be taken into consideration when the mode of application is chosen. For example, a highly viscous dipping lacquer cannot be sprayed or casted.

Furthermore, the striking differences between ester-soluble and alcohol-soluble types should be taken into consideration when nitro lacquers are formulated (Table 8).

For further information on the formulation of cellulose nitrate lacquers, see [52], [53].

**Dispersions.** Conventional cellulose nitrate lacquers contain between 60 and 90 % organic solvents, which are released during drying. For economic and environmental reasons, it is desirable to substitute organic solvents by water. Aqueous cellulose nitrate/softener dispersions (e.g., Isoderm, Bayer AG; Coreal, BASF; Waloran N, Wolff Walsrode AG) are available for such absorbing substrates as leather [54]. Other aqueous cellulose nitrate dispersions for use on wood, foil, and metal have also been developed (Waloran N, special-types, Wolff Walsrode AG) [55]. The film forming process of water-insoluble cellulose nitrate requires a small amount of coalescents in the dispersion systems.

**Celluloid.** A special use of cellulose nitrate is in the production of celluloid [56]. Cellulose nitrate with a nitrogen content of 10.5–11.0% is mixed in a kneader with softeners, particularly camphor, and solvents (alcohols).

Normal celluloid contains ca. 25–30% camphor and 70–75% cellulose nitrate. Celluloid that contains 10–15% solvent can be formed into the desired articles in heated piston or screw presses (e.g., tubes and round and profile rods).

1525

In the past decades, celluloid has been widely replaced by synthetic materials and thermoplastics. Celluloid is still of economic importance in the following areas: combs and hair ornaments, toilet articles, office supplies (drafting and measuring instruments), ping-pong balls, and various special uses.