

Nitrocellulose: Structure, Synthesis, Characterization, and Applications

Hisham Mattar^{1,2,*}, Zahraa Baz,¹ Ahmed Saleh,³ Ahmed S.A. Shalaby,³ Ahmed Elsayed Azzazy,³ Hesham Salah,³ Ibrahim Ismail^{4,5}

¹Zewail City of Science and Technology, 6th of October City, Giza 12578, Egypt.

²German University at Cairo, Faculty of Engineering, New Cairo, Egypt.

³Science and Technology Center of Excellence (STCE), Cairo, Egypt

⁴King Salman International University, Faculty of Engineering, Energy Engineering Program, El-Toor, South Sinai, Egypt.

⁵Cairo University, Chemical Engineering Department, Giza, Egypt.

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Abstract: Nitrocellulose is one of the most energetic polymers that have extensive importance in many vital applications. Nitrocellulose has proven itself, since it was accidentally discovered, and until now as a pioneering material of great properties that can be used in different fields without faltering.

In this review article, we will represent an in-depth outlook on Nitrocellulose: its chemical structure & properties, advanced ways of detection and its Nitrogen content, synthesis of some of its forms, and the different forms of applications. We have figured out that nitrocellulose is one of the materials that have characteristics ready for continuous enhancement where encouraging results are found.

Keywords: Nitrocellulose: Chemical structure, Degree of nitration, Characterization methods, Synthesis techniques, Nitrocellulose applications.

1 Introduction

The technological advancements of human civilization are always pushing boundaries and crossing them in all fields, urging to exceed and develop more than what was present and evolves quicker towards a greater destiny. Thus, people tend to always want to accelerate the development of their technologies, and what is acting as a major hindrance is the materials needed; the track of continuous development of materials. Since inventing new materials is rather complicated and laborious, people develop on already established materials and get greater results and benefits from them. From such developed materials is the Nitrocellulose, one of the greatest discoveries of the 19th century and versatile material of vast applications.

Nitrocellulose is considered one of the earliest derivatives of cellulose, aiming towards creating a flammable material by nitrating some cotton, sawdust, and starch. Baraconnaot in 1833 found the first form of it and called it Xyloidine. In 1838 T.J Pelouze used paper and cardboard and dipped them in highly concentrated nitric acid creating a more flammable product he called Pyroxyline. The Nitrocellulose as we know it is patented by C.F. Schnobein in 1846; using a mixture of sulphuric and nitric acid, he managed to increase the nitration and thus flammability and explosivity, creating Guncotton [1].

In this article, we have focused on the studies concerned with the nitrocellulose chemical structure, chemical, and physical properties and how its characteristics affect its stability and the application will be used in. Moreover, we have been interested in its thermal decomposition process and the detection methods as well as the synthesis techniques and its various applications.

2 Chemical Structures

To understand the chemistry of nitrocellulose we have to take a look at its parent polymer which is cellulose. Cellulose is a naturally created polymer of beta glucose where it has a glycoside linkage in carbon 1 and carbon 4 as shown in figure 1 [2]–[4].

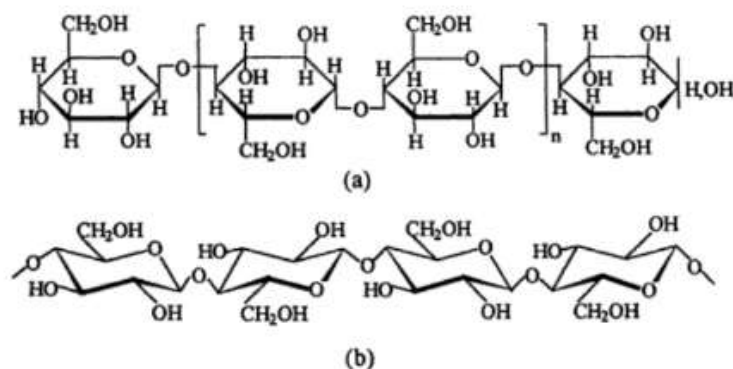


Fig. 1: (cellulose structure, a: Haworth formula, b: chair formula adopted from Polysaccharides in Medicinal Applications [2]).

Cellulose is produced through photosynthesis with an approximate amount of 1.3 billion metric tons annually. Cellobiose, which is made by two glucose molecules, is the base unit of cellulose. Cellulose has a basic chemical formula that depends on the degree of polymerization (p) and the chain units' number (n) and these two parameters mainly depend on the source of cellulose. Thus, the cellulose basic chemical formula is $(C_6H_{10}O_5)_n$, p [5].

Cellulose chains typically have a degree of polymerization with a range of 5000 to 7000 units of glucose monomer in the primary plant cell wall. However, cellulose produced from cotton and wood has a degree of polymerization of 15000 and 10000 respectively [6].

As noticed in the chemical formula the cellulose molecule is composed of carbon, hydrogen, and oxygen with an elemental percentage of 44.4%, 6.2%, and 49.4% respectively [5]. Along the cellulose polymer chain, each unit of glucose contains three hydroxyl groups that are ready for esterification [7].

Cellulose is available in an almost pure state in cottonseed hair and forms a native composite with lignin and other carbohydrates (hemicelluloses) in the case of wood cellulose, from which it is isolated by large-scale chemical processes of pulping, separation, and purification.

While wood is undoubtedly the most significant industrial source of cellulose, its production from plant fibers and crops such as flax, hemp, sisal, and others, especially from by-products of these various plants, is the dominant pathway for this material, which has become increasingly interesting. Bast (or stem or soft sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers are included in plant fibers [8].

If raw cellulose was put into an 18% sodium hydroxide aqueous solution, it will be divided into three types according to their solubility which are alpha, beta, and gamma. Beta and gamma types of cellulose dissolve in this solution, unlike insoluble alpha type. Treating this alkaline solution with acetic acid, the beta form will be insoluble and can be precipitated, unlike the gamma form which will remain in the solution. Beta cellulose is formed from oxycellulose and hydrocellulose and they have lengths of chain shorter than alpha cellulose which is called true cellulose. Gamma form is composed of hemicellulose [7].

Nitrocellulose is a nitrated ester of cellulose that is prepared by using a mixture of sulfuric and nitric acids for cellulose treatment. This reaction replaces the hydroxyl groups ($-OH$) with nitro groups ($-NO_2$) as shown in figure 2 [9]. All esters compounds derived from cellulose are organic except for nitrocellulose [7].

Nitrocellulose is a solid polymer which has no odor nor taste with a white appearance looks like that of cotton. However, It has a greater density [10]. Nitrocellulose with a wetting agent of 28–30 percent is comparable to cotton. Cellulose fibers, bamboo fibers, bagasse fibers, and cellulose derived from other stalk plants can also be used to produce refined cellulose and nitrocellulose using the similar process described above. The author researched the cotton pin, *Eulaliopsis binata*, bagasse, and other plant extracts and refined them into cellulose to prepare a thin paper that can be made after a nitration process to smokeless gunpowder nitrocellulose products [11], [12].

The nitrocellulose fiber morphology made from refined cellulose is very similar to that of refined cellulose. Similarly, the fiber morphology of nitrocellulose prepared from thin paper made from wood, bamboo, cotton comb,

willow grass, bagasse, and other plant extracts is still very similar to that of pre-nitration refined cellulose[11]–[14]. A white-yellow solid with an ether-like odor is pure nitrocellulose at room temperature. Industrial nitrocellulose, however, is normally not marketed in pure form but is dampened with water and organic solvents such as isopropyl alcohol, esters, ketones, or ethers of glycol. Damped nitrocellulose, depending on the amount of damping agent used, may be solid or liquid[15].

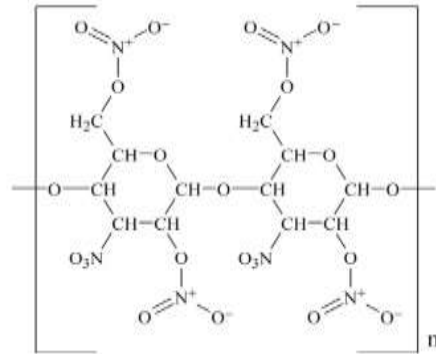


Fig. 2: (structure of nitrocellulose adopted from L. W. McKeen, “Environmentally Friendly Polymers,” Permeability Prop. Plast. Elastomers, pp. 287–304, 2012.[8]).

2.1 Degree of Substitution (Esterification)

The nitrogen content of cellulose, the nitrogen mass percentage found in the nitrocellulose molecule (N%), can be represented as a nitration degree or esterification degree. The nitration degree (NO ml/g) is the volume of released nitric oxide (NO) when the decomposition of one gram of nitrocellulose is completely done in the standard conditions (0 °C, 1atm).

The degree of substitution of nitrocellulose is a number that reflects the amount of exchanged hydroxyl groups expressed as “ γ ” and it can be calculated from the following equation [10]:

$$\text{Degree of substitution (DS)} = \frac{3.6 \times \text{nitrogen content (\%)}}{31.11 - \text{nitrogen content (\%)}}$$

Table 1: The relation between the three nitration degrees *

Nitrogen content %	Nitration degree (ml/g)	Degree of Substitution (Esterification)(γ)
10.37	165.4	1.79
10.75	171.46	1.9
11.13	177.52	2
11.46	182.79	2.1
11.97	190.92	2.25
12.44	198.42	2.4
12.9	205.76	2.55
13.28	211.82	2.7
13.61	217.08	2.8
13.75	219	2.85
13.88	221.29	2.9
14.14	225.53	3

* Table 1 (The relation between the three nitration degree forms adopted from J. Liu, Nitrate esters chemistry and technology. 2019[10])

Nitrocellulose DS is a property of high importance as it determines the application in which the polymer will be used [16]. Moreover, DS affects polymer solubility and viscosity[17]. Nitrocellulose with DS equals one, the lowest

value of the DS has a nitrogen content of 6.76%. theoretically, the highest value of DS is three which is corresponding to 14.14% nitrogen content. However, the maximum practically achieved DS was 2.9 which is a polymer with nearly 13.9% nitrogen content [18] as the synthesis of these highly nitrated products is costly and hazardous due to unstable product formation. The density of nitrocellulose increases with the increase of its nitrogen content [19].

The solubility of nitrocellulose is directly affected by the degree of substitution and the degree of polymerization in an inversely proportional manner[18]. It was proved that the nitrocellulose viscosity is directly proportional to the degree of substitution. Moreover, the degree of polymerization of cellulose has a great effect on the degree of substitution and accordingly the nitrocellulose intrinsic viscosity. The intrinsic viscosity increases with the increase of the degree of polymerization[7].

The higher the degree of polymerization, the higher the increase in intrinsic viscosity with increasing nitration observed. But cellulose derived from different sources and having varying degrees of polymerization, nitrated to the same level may have significantly different viscosities intrinsic to each other[20].

Solubility decreases as the Nitrocellulose content decreases. Thus, although low-nitrated nitrocellulose (DS 1.9–2.1) is soluble in alcohols, esters, ketones, and glycol ethers, high-nitrated nitrocellulose (DS 2.1–2.4) are insoluble in formulations of alcohol, although it may be dissolved in esters, ketones, and glycol ethers[21].

In comparison to solubility, as the nitrogen content of nitrocellulose and the concentration of nitrocellulose solutions increases, the viscosity increases accordingly [21]–[24].

Moreover, the nitrogen content increases directly proportional to the nitrocellulose explosion heat. However, the nitrocellulose specific volume, formation heat and combustion heat inversely proportion with the nitrogen content [10]. When the nitrocellulose nitrogen content increases the compound stability decreases due to the repulsion forces of the electronegative groups found on the base rings [25].

Due to the difference in the degrees of cellulose polymerization and the characteristics of the cellulose reaction, the nitrogen content, the degree of polymerization, and the distribution of the nitrate group in the NC macromolecules prepared under normal nitration conditions are different. For example, there are 1039 different substitution patterns according to the calculation for NC having an average degree of cellulose polymerization of 100 and the average degree of substitution of each link of 1.5. Hence the heterogeneity of NC is far more complex than that of cellulose; only the completely substituted trinitrate of cellulose is chemically homogeneous. The average degrees of nitrocellulose polymerization of No. 1, No. 2, and No. 3 for gunpowder production are usually 500–700, 700–1000, and 250–400, respectively, respectively[26].

NC with a nitrogen content of 7% or less still exhibits the characteristics of swelling cellulose; NC with a nitrogen content of 8.99% exhibits a mixed character of natural cellulose and trinitrate cellulose; where NC has a nitrogen content of 12.73% or more, NC exhibits only the characteristics of cellulose trinitrate after a stable procedure. This finding also indicates that when the degree of nitration of cellulose-derived nitrocellulose is less than or equal to approximately 1.00, the structure of the molecular group of NC has no substantial difference from that of cellulose; where the degree of nitration is between 2.00 and 2.25. When the nitration degree is 2.50, the structure of NC is typically irregular with a possible small amount of unevenly distributed hydride, decreased intermacromolecular interaction, and increased flexibility[14]. It has also been observed that thermal stability decreased as the nitrogen content increased[27].

2.2 Nitrogen Content and Applications

Nitrocellulose can be classified based on many properties, in the following table, table 2, simple classification is made upon the nitrogen content[28].

2.3 Degradation of Nitrocellulose

NC is a highly flammable solid, known to quickly ignite and explosively burns if a heat source is added to it, the vapor from the nitrocellulose along with the oxygen in the air will catch fire at low temperature as low as 13°C. Is as well notorious for spontaneously igniting without an external spark or flame when the temperature is increased to 160-170°C and above[15]. Since it is a crucial ester to many industries and applications, researchers have been interested in the kinetics and thermodynamics of nitrocellulose degradation especially for explosives as these characteristics are of high importance for manufacturing safety, storage, and final application. Thus, continuous research has been developed to study different degradation techniques of explosives which include thermal, mechanical, and biological processes[18].

Table 2: classification of Nitrocellulose upon their nitrogen content **.

Grade	Nitrogen Content	solubility	Properties and Application
A	10.7%-11.3	soluble in ethanol and esters[29]	Show thermoplastic behavior which is important for foils and films used in heat sealing. Used in printing inks application due to the high solubility in alcohol. Its coatings have a low odor.
AM	11.3%-11.8%	partially soluble in ethanol and esters	Show mixed characteristics from that of the A and E grades Used in staple coatings or the cellulose films coating
E	11.8%-12.3%	soluble in Esters more resistant to alcohol	Show excellent mechanical properties thus, it is used in forming hard films. Their solvents evaporate rapidly. Used in military applications and propellants

** (Table 2 classification of Nitrocellulose upon their nitrogen content adopted from Dow Wolff Cellulosics, "Walsroder Nitrocellulose Essential for an Extra-Special Finish," p. 60, 1998 [28])

2.4 Thermal Decomposition of Nitrocellulose

Degradation of NC is usually done through thermal processes. Its degradation using thermal processes is comparable to the thermal decomposition of organic peroxides[7].

The degradation reaction of nitrocellulose starts with the scission of O-NO₂ bond to release NO₂ which immediately complexing to form nitrate group (CONO₂) that is rapidly involved in a reaction to produce oxidation products [30]. Water presence in the surrounding environment or the nitrocellulose promotes a hydrolysis reaction of the O-NO₂ bond to produce nitric acid (HNO₃) which accelerates the reaction, catalytic action, to release more NO₂ that led to cyclical pathway generation and uncontrolled consequences of self-heating[19][31][32]. Moreover, the uncontrolled generation of the NO₂ makes this reaction an autocatalytic one that may result in a dangerous situation if stabilizers such as diphenylamine are not used to scavenge NO₂ groups generated[7].

Under normal temperature and pressure, nitrocellulose is stable. It is, however, shock-sensitive and can break down to create poisonous gases such as nitrogen oxides and carbon monoxide upon heating. Both dry and damp nitrocellulose react easily to create nitrogen oxides with strong oxidizing agents, including strong acids and bases and such the need for stabilizers[15].

Traditional stabilizers can be generally categorized into urea derivatives and aromatic amines, such as Akardite-II, N-methyl-4-nitroaniline diphenylamine, and 2-nitro-diphenylamine[33]. Previous studies have proven that the reaction of traditional stabilizers such as N-nitrosodiphenylamine with nitrocellulose forms carcinogenic products [34].

The effects of humectants on NC's thermal stability, microstructure, and combustion characteristics were studied by He et al, which demonstrated that NC with isopropanol and ethanol humectants showed small variations in their microstructures, but the former had a greater risk of fire[19].

Green stabilizers, such as curcumin and guaiacol, are proposed as substances that can replace the normal stabilizers without the creation of any measurable number of products derived from CMR[35]. Curcumin can be extracted from the turmeric roots (*Curcuma longa*) and has been identified as an excellent receptor of the -NO₂ groups [36]. Guaiacol is a natural substance found in weed leaves of guaco or witch (*Mikania glomerata* Spreng.) and has been shown to interact with the atmospheric nitrite to create 4-nitroguaiacol, 6-nitroguaiacol, and 4,6-dinitroguaiacol[37]. The suppression of nitric oxide oxidation by curcumin to nitrite is due to the sequestration of the intermediate nitrogen dioxide reaction and not to nitric oxide[36].

A study was done to discuss how the thermal characteristics and microstructure of nitrocellulose are affected by its nitrogen content. In this study, the Arrhenius equation and a developed theoretical model was used to obtain the activation energy and the heat of reaction and other relevant thermodynamic parameters of nitrocellulose passed by

a low heating rate decomposition process which allowed the authors to obtain the turning point, the point where the sudden increase of the released heat occurs, of the nitrocellulose heat flow curve[38].

In another analysis, the thermal behaviors and microstructures of microsized and nanosized NC were compared and this proved to be more dangerous for the nanosized NC. The respective kinetics were also obtained using ASTM E969 and the Ozawa process[39].

Theoretical and experimental studies have been performed to discover the effects of nitrogen content on nitrocellulose thermal characteristics under low heating conditions. In the study of NC decomposition kinetics, C80 calorimeter, a kind of thermal analysis tool, was used isothermally and non-isothermally[40].

Samples of nitrocellulose with different nitrogen content were studied using a scanning electron microscope where the results proved that high nitrocellulose with high content has more cracks and fibrous structure with coarser surface and these characteristics enlarge the reacting surface area which has direct contact with the air and this promotes the reaction completion. Moreover, the decomposition reaction activation energy and the critical explosion temperature are reduced by elevating the nitrocellulose content of nitrogen. Thus, more attention is required for nitrocellulose with high content to assure safety during its whole life cycle [38].

Previous research stated that nitrocellulose can have an effective storage life of up to 10.57 years at ambient temperature without degradation[41].

Aging was also investigated to study its effect on NC stability and shelf life.

Kennedy et al. examined NC's aging mechanism in plastic-bonded explosives. They submitted that kinetics follow Arrhenius-type linear action and that the kinetic parameters can be determined over the temperature range from 40 to 70 °C by the random chain scission model[42].

Brill and Gongwer suggested that the slow decomposition of NC would occur when the ambient temperature is in the range of 50–100 °C, and the secondary products may release a small amount of NO_x[43].

Wei & et.al found out that as the aging period increases, the patterns in thermal kinetic parameters for pure NC first decrease and then increase sharply from 24-day aging to 32-day aging, suggesting that pure NC has the highest risk when aging for 24 days[44].

Chai & et al performed some experiments concerning the NC stability as well and the results showed that the heat of reaction (DH) of the four samples increased with the increase in nitrogen content, which meant greater nitrogen content could result in greater heat release[38].

2.5 Synthesis Techniques of Different Forms

The synthesis of nitrocellulose is predominant on many factors: the cellulose itself meaning the source from which you prepare the solution, the acids added to nitric acid to aid in the nitration process, the condition of the reactions themselves being the temperature, pressure, or different chemicals added to stabilize or catalyze the reaction. All these factors affect the shape, structure, function, and behavior of the Nitrocellulose after preparation and during application.

The most general way of producing the nitrocellulose would be as follows: A portion of fine cotton wool to be dissolved in 15 sections of the same sulphuric and nitric acid mixture. The cotton was stripped and washed in cold water after two minutes to set the esterification level and remove all the residue from the acid. It was then dried gradually at a temperature around 40 ° C

Researchers also studied the different results that would come out of treating the cellulose fibers with a different nitrating solution; using another solution with nitric acid.

Table 3 Preparation methods for nitrocellulose^{***}

Nitrating agents	Ratios	Max Nitrogen %	Comments
Nitric Acid only		<ul style="list-style-type: none"> 8% 13.6-13.8% when treated by vapor first then 98% concentrated Acid 	<ul style="list-style-type: none"> gelatinization of surface fibers upon contacting the acid. No Industrial use so only done in labs Easy to stabilize
Nitric Acid, Sulphuric Acid, and water	2:3:3	<ul style="list-style-type: none"> 13.92% 	<ul style="list-style-type: none"> Decreasing water induces swelling and reduces the rate

			<p>of the reaction</p> <ul style="list-style-type: none"> Increasing water decreases the nitrogen content Increasing Sulphuric acid slow the reaction as well
Nitric acid and Phosphoric acid	1:1 to 1:3	<ul style="list-style-type: none"> 13.7% 	<ul style="list-style-type: none"> Extremely stable, no phosphoric esters Deviation away from the composition of the nitrating mixture had an effect of crystallizing or hardening the fibers.
Nitric acid and acetic acids/acetic anhydride		<ul style="list-style-type: none"> Over 14% 	<ul style="list-style-type: none"> Three extractions by boiling alcohol to stabilize The potential formation of acetyl nitrate (explosive at high temperatures)
Nitric acid and Organic Solvents (Carbon tetrachloride, methyl nitrate, or Chloroform)	Using Methylene chloride and Nitric acid, raising the nitric acid to 25%	<ul style="list-style-type: none"> 13.4% 	<ul style="list-style-type: none"> The polymer chain was not degraded by the nitration process which leads to improved mechanical properties

***Table 3 (preparation methods for nitrocellulose adopted from C. García-Ruiz, "Nitrocellulose in Propellants," no. January, 2012 [17].)

The source of cellulose in the previous reactions was usually wood pulp or cotton, as it provides the greatest percentage of alpha-cellulose that can be extracted and then used accordingly in producing nitrocellulose[18].

2.6 Analysis and Measurements of Nitrocellulose

One of the most important factors that affect the properties and applications of the nitrocellulose is the degree of Nitration, the amount of nitrogen content available in the final product. When nitrocellulose has a low degree of nitration, it is used in medical and industrial applications such as paints. However, when nitrocellulose has a high degree of nitration, more than 12.5%, it is applied in explosives and it becomes thermally unstable [18][31] and it exhibits some unusual hazardous properties such as high vulnerability to impacts, low chemical stability, flammability, and explosive hazards. In particular, heat accumulation can occur in the NC system if the heat output rate is significantly higher than the heat release rate and thermal runaway eventually will occur[45].

Therefore, it is imperative to always have a way to determine the nitrogen content easily and safely to be used in its correct application. This is usually done by a process of denitration, which can be obtained through alkaline or acid hydrolysis. NC acid denitration is however much slower than alkaline hydrolysis[46].

The reference method for this determination to date is still the long and repetitive Devarda process, based on alkaline denitration of NC in the presence of hydrogen peroxide, reduction of nitrate ions released into ammonia by Devarda alloy, and back-titration of sulfuric acid added by sodium hydroxide to excess ammonia. The Devarda alloy being an alloy of aluminum (44% – 46%), copper (49% – 51%) and zinc (4% – 6%) [47], [48].

Due to it being a long and tedious technique, advanced processes have been developed to shorten the testing time and get more accurate results. From these processes:

- Alkaline hydrolysis
- Ion chromatography
- Capillary electrophoresis
- Gas Chromatography-Electron Ionization-Mass Spectrometry (GC-EIMS)

2.7 Alkaline Hydrolysis:

Alkaline hydrolysis is a process of denitration of nitrocellulose, removing nitrite and nitrate ions from the specimen. It is usually used accompanied by other techniques for nitrite and nitrate ions analysis such as ion chromatography (IC) and capillary electrophoresis (CE).

The alkaline hydrolysis process first adds a certain hydroxide solution to NC. Multiple pieces of research tried different hydroxides, and results indicated that NaOH and KOH are more effective at comparable concentrations than $\text{Ca}(\text{OH})_2$ and NH_4OH s [49]. Therefore, the process is usually done using a solution of sodium hydroxide added to the dried nitrocellulose, then the mixture is heated for a fixed time in a block heater. After the hydrolysis is finished, the sample is put into an ice bath to cool down then allowed to rest at room temperature. In some experiments to satisfy certain volumetric conditions, the solution would be transferred to a flask and then supplemented with ultra-pure water to fulfill the required volume and concentration [50]. Moreover, this process can be used as a method of treatment for the waste of nitrocellulose [51].

2.8 Ion Chromatography

Ion chromatography is a method to separate the dissolved inorganic ions. The separation process is done through three columns of different ion exchange media where the sample is eluted into a conductivity cell where the separated ions are detected. The first column which is called precolumn, guard column, and the second column which is the separation column are packed with an exchange resin of a strongly basic anion. Based on the tendency to exchange with the resin ions, the sample ions are separated. The third column is used to suppress the effect of the mobile phase conductivity to reach a negligible level and ensure that the anions have been converted into their basic acid forms. The electrical conductivity cell is used to measure the concentration of the separated ions in the corresponding acid forms. The identification of ions is accomplished upon comparing their retention times (RTs) to the retention time in the calibration standards. However, the ions concentration is measured by comparing the area of the measured curve to the standard calibration curve [52].

To use this technique in the nitrogen content identifying for nitrocellulose sample previous research was done on a sample isolated from gunpowder where the isolated nitrocellulose passed by denitrification process, alkaline hydrolysis, to release the nitrite and nitrate ions then the hydrolyzed filtrate is ready for the chromatography analysis to determine the total mass of nitrogen in the sample. Gravimetric measurement is used to determine the mass of the nitrocellulose sample so that the ratio between the total nitrogen mass and the mass of nitrocellulose is obtained. This ratio is the nitrogen content [53].

2.9 Capillary Electrophoresis (CE)

Electrophoresis is the process where charged particles, ions, are separated upon applying a suitable electric field. The electrophoresis system is mainly made up of opposite charge electrodes, anode, and cathode, connected by an electrolyte which is a conducting medium. Variations in the velocity of particles result in the separation of ions. The particle velocity (v) is the product of electrical field strength (E) and particle's mobility (m). The mobility of a specific particle is affected by its shape, size, and charge. Moreover, the separation temperature affects the mobility of the particle. However, the mobility of one particle is constant while conducting specific electrophoretic conditions [54].

Capillary electrophoresis (CE) is widely used as a simple alternative to IC for inorganic ion analysis, in particular in the environmental field. CE was already documented for nitrite and nitrate ion determination. Since both anions' absolute mobility is very similar, acidic context electrolytes are preferably used to take advantage of the nitrite anion's weakly acidic properties. Compared to IC, the use of CE for nitrite and nitrate ion analysis offers advantages such as easier sample preparation, shorter processing cycles, miniaturized operating conditions, and much lower running costs [24], [50], [55].

In capillary electrophoresis, the electrophoresis process takes place in a small capillary that has an inner diameter range of 20 to 100 microns. The Capillary electrophoresis is considered an effective technique to dissipate heat produced from the applied electric field because of the high surface-to-volume ratio of the capillary. The separation time needed in capillary electrophoresis is very small due to applying high electrical field and voltage [56].

To determine the concentration of nitrite and nitrate ions released after nitrocellulose hydrolysis the external calibration method of standardization with aqueous standard nitrite and nitrate ion solutions was performed. Molybdate anion was used as a standard for internal use. The nitrogen content is determined through a relationship between the concentrations of nitrite and nitrate ions in mg/L, f the dilution factor, M the molecular mass, V_{NaOH} the

volume of sodium hydroxide in mL, m_{NC} the amount of dry NC in gram, and η the denitration yield[57][50]

$$\% N \text{ experimental} = \frac{\left(\left(\frac{[\text{NO}_2^-] f M_N V_{\text{NaOH}}}{M_{\text{NO}_2}} \times 10^6 \right) + \left(\frac{[\text{NO}_3^-] f M_N V_{\text{NaOH}}}{M_{\text{NO}_3}} \times 10^6 \right) \right)}{m_{NC} \times \eta} \times 10^4$$

Figure 3 Nitrogen content from CE

2.10 Gas Chromatography-Electron Ionization-Mass Spectrometry (GC-EI-MS)

Gas-chromatography and mass spectrometry are analytical methods that are used in identifying different substances in one sample. Gas Chromatography-Electron Ionization-Mass Spectrometry (GC-EI-MS) is an advanced analytical method that combines the characteristics of gas-chromatography and mass spectrometry where an electron beam is used for the ionization process [58].

This technique is usually used to detect particles in explosives especially smokeless gun powders which usually contain nitrocellulose. Due to its non-volatility, Nitrocellulose cannot be detected using GC-EI-MS, unlike all the organic explosives and additives. The research was done to come over this problem by finding out the new preparation method used before the analysis process. The novel preparation method is done in three main steps:

- 1- Using acid hydrolysis to breakdown nitrocellulose into glucose residues, Nitrocellulose is the only explosive compound that is made up of glucose residues.
- 2- Methanolysis and glycoside residue trimethylsilylation (GRT)
- 3- The obtained volatile derivatives of the trimethylsilylated methyl glycoside are classified using GC-EI-MS[59][17].

3 Applications

3.1 Military Applications

Nitrocellulose with high nitrogen content, 12.95% - 13.35%, is usually called gun cotton to express how this material is explosive and highly flammable[60][61].

NCs are often present in gun powders typically categorized by the number of energetic materials in their formulation: (i) single-base propellants containing predominantly NC, (ii) double-base propellants consisting of NC and nitroglycerin, and (iii) triple-base propellants containing NC two other explosive substances (nitroglycerin or dinitroethylenglycol and nitroguanidine). Types of said explosive materials can vary; one of them is dynamite (which is an explosive mainly for civil purposes), another type is propellant or most commonly known as gun-powder (which is an explosive utilized to move projectiles at rapid speeds)[62].

Continuous development is in progress to improve its properties such as increasing its stability and burn rate. Researchers have developed an improved preparation technique of sub-micron nitrocellulose to reach particles with the low activation energy for the decomposition process, a 350% greater burn rate, and characteristics to achieve complete combustion[63].

To increase the nitrocellulose burning rate another research was done to study the effect of doping nitrocellulose microfilms with Graphene Oxide (GO) within the range of 0.5-3 wt%. when the combustion behavior and the laser ignition of the mixture were studied by digital high-speed imaging and Nd: YAG laser, the researchers found that the burning rates and laser ignition have outstanding improvement if 0.5% or more of GO doping was used. Moreover, the doped nitrocellulose films showed to be more thermally stable than traditional nitrocellulose due to the increase in decomposition activation energy[64].

Another way is by a catalytic change in macrostructure and changing the geometry of the shape itself. A flammable composite, solid composite propellant AP-NC (Ammonium Perchlorate Nitrocellulose) got its flammability enhanced by a magnitude of 7 times in bulk value, and its activation energy reduced by 25%; this was feasible using a 3-D, highly conductive, interconnected, porous and CuO (Copper Oxide) - functionalized GF (graphene foam) micro-structures. The Graphene foam structure itself distributed and conducted the heat more efficiently than without it thus increasing the burn rate, the addition of CuO acted as a catalyst to the burning yet had a negative effect as well; as it needed some of the exothermic energy to get heated up. An optimum loading of both GF and the CuO was determined, 10% and 3% respectively[65].

NC can also be used to enhance the properties of other explosives like creating nanothermites using the coating of NC on the surface of Al/Bi₂O₃, which in term enhances the properties of Al/Bi₂O₃; giving it more stability by improving the ESD (Electro Static Discharge) safety, and enhancing the combustion reaction, heat release, and pressurization. The NC was added to Al/ Bi₂O₃ in different weight percentages using Electro spraying techniques to create the composite and they were compared to each other and to a common primary explosive called LTNR (Lead styphnate). The optimum weight percentage found was 3wt% NC which showed superior stability, highest energy output, and greatest combustion[66].

3.2 Medical Field

Nitrocellulose has proven itself being greatly beneficial and versatile in the medical field; facilitating previously laborious operations, increasing the accuracy & efficiency of tests, and providing some novel techniques to detect changes in the human body.

First, Nitrocellulose is used greatly and investigated in the application of biosensors and chips that can detect different antibodies, proteins, serums, and other chemicals that affect the homeostasis of the body. Nitrocellulose can be used as an adlayer on the sensor chip of the MCLW optical biosensor; this was to reach a label-free detection of the CRP in human serum and for easy immobilization of antibodies on the chip[67].

Allergies and allergy-producing chemicals is a field where Nitrocellulose was also investigated. The test is usually used to check for allergies and find their triggers is the radioallergant test (RAST), usually, cyanogen bromide activated paper is used in it, however, research proved using Nitrocellulose sheets is more effective[68].

Properties and characteristics of such films and membranes can also be improved by various techniques. Polysaccharides (both bacterial and neutral) adhered to NC in a new novel technique called Vacuum filtration. The resulting film can be used as Blotting assays examining specific types of antibodies. The process itself being simple, quick, and efficient makes it a great advantage and of great prospect[69].

Because of their high protein-binding affinity, compatibility with a variety of detection techniques, and the ability to immobilize proteins and glycoproteins, nitrocellulose membranes are a common matrix used in protein blotting. Nitrocellulose membranes may also be used: southern and northern blots, amino acid analysis, western transfer, and dot/slot blots. There is a protein-binding potential of 80 to 100 $\mu\text{g} / \text{cm}^2$ for nitrocellulose membranes. Protein immobilization is thought to occur through hydrophobic interactions, and during electrophoretic transfer, high salt and low methanol concentrations boost protein immobilization to the membrane, particularly for proteins with higher molecular weights. Due to the high efficiency of irreversible protein binding, nitrocellulose membranes remain a common option [70].

From the methods used to improve protein blotting a novel technique of Phosphorylation and assay of a phosphoprotein. In the research proteins are extracted from tissue samples, used in solution form, separated by polyacrylamide gel electrophoresis then immobilized on Nitrocellulose membrane filters. The protein blotting on NC can be efficiently phosphorylated due to the great concentration on the very thin layer[71].

NC can also be utilized in point-care biosensing. Investigating its usage in Lateral Flow Assays (LFA), NC membrane with electrospun Polycaprolactone (PCL) fibers enhanced the LFA sensitivity by 10 folds [72].

Nitrocellulose is also utilized in different ways in the medical field. It has been investigated whether Nitrocellulose bandages can be effective in wound healing especially hard to cover wounds, and thus nitrocellulose liquid bandages were produced with nanopores to be used in hard-to-cover wounds. The nano-porosity showed an enhanced antibacterial effect, an increased time of healing, and non-toxicity on the wound itself [73].

Fields of medicine and enzyme carriers using NC have been investigated as well. Using Nitrocellulose with Magnetite to create magnetic microbeads. NC dissolved in acetone and dichloroethane with the magnetite particles immersed in them and using a special solvent evaporation technique the magnetite is completely covered with the NC microbeads. The results show great potential in the magnetic carrier technology field; having hydroxyl groups available on the surface of the beads allowing for easy activation and enzyme mobilization[74].

3.3 Industrial Applications

Other than the medical field, Nitrocellulose has proven itself versatile and beneficial in many other fields; including water filtration, electricity generation, catalysis, and coatings.

Biosynthesized silver nanoparticles were impregnated in the Nitrocellulose membrane filter to study its effect on bacterial filtration and inhibition of bacterial growth. Silver nanoparticles biosynthesized from *Aspergillus niger* (AgNPs-Asp), *Cryptococcus laurentii* (AgNPs-Cry), and *Rhodotorula glutinis* (AgNPs-Rho) were all obtained, in addition to chemical Silver nanoparticles to be impregnated in the Nitrocellulose filter. The bacteria used to test the

effectiveness were *Escherichia coli*, *Enterococcus faecalis* (both used or found generally to show fecal contamination), and *Pseudomonas aeruginosa* (a pathogen that can grow on the water surface and pipes). For AgNPs-Rho, a higher antimicrobial effect was observed. This will refer not only to the smallest particles but also to the classes of polysaccharides surrounding these particles.

Besides, on nitrocellulose membrane philters impregnated with 1 mg L⁻¹ of biosynthesized AgNPs, complete inhibition of bacterial growth was observed in this study. This concentration was able to minimize the colony count of bacteria by more than 5 orders of magnitude, making it ideal for a system for water purification[75].

Paper-based Triboelectric nanogenerator (P-TENG) is a way of generating a sustainable form of green electronics, that works by utilizing different triboelectric polarities and thus generate a current and voltage. Here in this paper, a discussed form uses crepe cellulose paper (CCP) with Nitrocellulose membrane (NCM) as friction layers of the P-TENG. Great values of voltage, current, power, and robustness were achieved. The introduction of NCM as the negative triboelectric material highly enhanced the properties of P-TENG to reach voltage outputs of about 194 V (when paired with CCP as positive triboelectric material and layered in 3 layers)[76].

When the nitrogen percent is lower than the military-grade, the graphene oxide (GO) doping is utilized to form other important products and even composite materials. To form a composite material, GO can be readily dispersed in the NC matrix and the rich nitrogen in NC can be used as a source of nitrogen to react with GO at a high temperature to prepare NGs. In recent years, the preparation of nitrogen-doped graphene (NG) has received attention because the incorporation of nitrogen into graphene's carbon lattice can modulate the intrinsic properties of graphene by the electron donor or acceptor and improve the chemical functionality and electrical properties of graphene, such as the specific capacitance and cycle ability. The original GO-NC hybrid materials are soft and versatile and can be easily manufactured in various sizes and shapes, enabling the size and shape of the N-doped 3D graphene networks to be modified. Besides, on various substrates, such as indium tin oxide (ITO), metals, glass, silicon wafers, and mica papers, the N-doped 3D graphene networks can also be prepared by depositing and burning initial GO-NC hybrid materials on these substrates. This is a simple method of obtaining modified electrodes or substrates from the N-doped 3D graphene network. Therefore, there are different potential applications for the N-doped graphene networks prepared by this simple combustion process, including energy storage and conversion, catalysis, and sensors[77].

Nitrocellulose has been used in many coating applications as well; as part of the coating itself, a stabilizer, a membrane for the coating, and others. It is widely used in paints, lacquers, varnishes of wood, paper, and metal, inks for package printing, and celluloid printing.

Modern lacquers are cellulose nitrate solutions that were introduced in 1925. Through evaporation of the solvent, these coatings dry. Pigmented lacquers of nitrocellulose were used as automotive finishes in 1913. In the 1940s, cellulose nitrate lacquers with greater solid quality were hot-sprayed. Cellulose nitrate coatings were improved in the 1950s by the production of multicolor lacquer enamels and superlacquers based on cellulose nitrate-isocyanate prepolymers to meet competition from alkyd-amino resin coatings. Nitrocellulose was the basis of wood lacquers, but its use is diminishing. Nitrocellulose-compatible Alkyd resins have been used for plasticizing nitrocellulose lacquers[78].

The NC as a solid material is hardly used in coatings, but mixing it in amyl acetate and industrial wood alcohol creates pyroxylin, which is then used in the manufacture of lacquers, waterproofing solutions, leather structures, and artificial silk. The content of nitrogen ranges from 10.5-12.2 percent. Pyroxyline lacquers usually consist of mixtures consisting exclusively of Pyroxyline for the total solid matter, but typically containing bronzing liquids, often containing a limited amount of resin. Other types of similar lacquers can be for example resin lacquers, "wrongly referred to as" gum lacquers "and not containing Pyroxyline." They are resin and gum resin solutions in fuel oil and pyroxylin solvents, not containing linseed or other drying oil or turpentine, and are thus not called varnishes if the term is accepted correctly. Finally, 'Lacquers of pyroxylin resin,' a mixture of the two groups referred to above[79].

Arranged more accurately in terms of their implementation strategies, the two subdivisions, dip and brush lacquers, inevitably crash. Dip: One that provides the greatest tenacity and covering power with the least residue accumulated is the perfect dip lacquer. They deposit a uniformly smooth, clear, lustrous, and elastic film on the most highly polished surface and closely grained metal, possessing great tenacity, and which in no way alters the appearance or impairs the luster of the surface on which it may be applied. Often NC with content that evaporates. Brush: intended primarily for embellishment, as opposed to dip coatings intended solely for safety, either resin alone or in combination with pyroxylin[79].

Other applications for the pyroxylin would be the manufacturing of Bronzing liquids; Bronzine, Aurum, Argentine, Silverine, Lustrogen, and Japanese, Chinese and Oriental Gold Paint are variously regarded as the class of pyroxylin lacquers used as a medium for the application of aluminum and bronze powders Adding more resin, more oils, other

additives change the lacquer properties and allow for new previously unattained properties. Like for example creating heat-resistant Bronzing liquid; boiled linseed and other drying oils are added and the resin is increased[79].

Antifouling coating and lacquers are also produced used pyroxylin. These coatings are intended for use on the bottoms of ships to minimize the accumulation of barnacles and marine vegetation. These lacquers cling to the metal plates tenaciously, are unaffected by the mineral constituents in marine water, and serve as an important defense against the invasion of 'borers' and other wood-destroying mollusks in wood-bottom vessels. The lacquer is typically Pyroxylin solution, containing anti-septic and fungicide constituents such as naphthalene, with or without a small amount of resin added, salicylic acid, phenol, mercuric and cupric salts, cresols hydrazine, hydroxylamine, weak acids, or other compounds[79].

NC is also currently utilized extensively in wood coatings; which are coatings and lacquers and coatings used to enhance the ascetic properties of wood products, improve the surface finish and increase the lifetime and longevity of the product. A company utilizing this concept uses a fast-drying system with excellent quality in combination with nitrocellulose resin, and such NC sanding sealer and NC varnish were introduced for the interior house and office furniture. For either the sealing application or the varnish application, a 20% solution of NC is used and it is 50wt% of the lacquer. The lacquer was unique for its high mechanical strength, hardness, and transparency with a very fast drying time[80].

Creating a superhydrophobic coating (SHC) fabricated on NC lacquer in a single-step spraying method. Using the sol-gel method; the suspension of perfluoro silane coated nanoparticles of silica was fabricated at temperatures of 60 degrees Celsius and then directly sprayed on Nitrocellulose lacquer substrates. These types of coating can be greatly beneficial in the applications of metal protection from corrosion, stain-resistant, and anti-biofouling paints. What makes this technique unique is first the utilization of NC lacquer making it easy to fabricate and open up multiple applications that were not prior reachable like electronics and optics, second the fabrication temperature, and the hydrophobic properties of the coating; keeping its mechanical and chemical properties/structure even after treatment with water, bases, acids and leaving it in the outdoors. Third, the SHC is well known for its excellent longevity and chemical stability with adequate adhesion to different materials, extending the service life of the nitrocellulose lacquer by retaining its characteristics[81].

4 Conclusions

When studying the literature of nitrocellulose, we have concluded that this area of research is very dynamic, and that nitrocellulose has proven itself to be vital material with unique properties that can be applied in many fields. Going through its properties, synthesis techniques, and various applications, we have wondered what can be next for this material.

Further work should be done in exploring the promising characteristics of this material so that we can reach a more stable form of it. Moreover, we will work on improving the novel economic process of nitrocellulose production in Egypt. This process will depend on agricultural waste as a source of cellulose.

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