PRODUCTION OF NITROCELLULOSE RESIN FROM COTTON

BY

MAKWASHI NURA 75%

(2005/21690EH)

SUBMITTED TO

DEPARTMENT OF CHEMICAL ENGINEERING
FEDERAL UNIVERSITY OF TECHNOLOGY,
MINNA, NIGERIA.

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE BACHELOR OF ENGINEERING (B. ENG) DEGREE

AUGUST, 2009.

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DECLARATION

I, MAKWASHI NURA declare that this research project is solely the result of my work and has never been submitted anywhere for any dilemma, neither someone has done it for me.

Credit should go to the writer whose work appears in the reference of this project.

NURA MAKWASHI

Student's name

20/09/09

Signature

APPROVAL

This is to certify that this project is an original work undertaken by **MAKWASHI NURA** with Matric no. **2005/21690EH** and has been prepared in accordance with the regulations governing the preparation and presentation of project in Federal University of technology, Minna.

Date: 06/09/2009

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Date: 07/09/09

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Date: 5/03/2010

External Supervisor

DEDICATION

This research project is dedicated to almighty Allah, my creator and maker for his divine favour, mercies and protection given to me during the course of this work and also to my father and mother Alh. (Hon.) Makwashi Abubakar and Haj. Fatima Makwashi thanks for given me the support and encouragement.

ABSTRACT

The main aim of this project was to produce nitrocellulose resin from cotton (which forms a lacquer used in preliminary stages of wood finishing developing a hard finish with a deep luster, Printing inks and in leather finishes).

During the experiment, nitric acid ($HNO_{3(aq)}$) and sulphuric ($H_2So_{4(l)}$) acid were used as the nitrating agent while cotton was used as cellulose($C_6H_{10}O_{5(s)}$), sodium bicarbonate solution and distilled water were used to neutralize the acid content in the cellulose nitrate and acetone ($(CH_3)_2CO_{(l)}$) was used in transforming the product to a concentrated syrup-like nitrocellulose lacquer. Two by three (2×3) factorial designs was used to carry out the experiment in which two parameters were considered to be changing at three different experiments each.

The nitration time obtained during the whole experiment are 5.0, 6.0, 6.0 and 8.0 minutes for the first parameter that changes from a volume of 70, 60, 50 and 40 ml and 5.0, 5.0 and 5.0 minutes for the second parameter that also changes from 60, 50 and 40 ml respectively. The total volume of the product obtained, volume of sulphuric acid used and volume of nitric acid used was were 105~~ml~~, 430~~ml~~ and 430 ml respectively, the details of this results were summarised in Table 4.0.

Conclusively, the final product obtained which is yellowish white product and burns all at once with a fast bright flame and does not produce any smoke, shows that all the experiment carried out yield a required product and was tested to be within the standard.

It was recommended that wood pulp should be tried instead of cotton wool so as to compare the quality of the product obtained.

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CHAPTER ONE

1.0 INTRODUCTION

Nitrocellulose (also: “cellulose nitrate”, ”flash paper”, "Collodion Wool", "Soluble Gun Cotton", "Iodion Cotton", "Pyroxylin", "Colloxylin" "Xyloidin", "Celloidin" "Parlodion") is a highly flammable compound formed by nitrating cellulose through exposure to nitric acid or another powerful nitrating agent. Nitrocellulose is a product that has found many uses on everyday life. It is a white, yellow or transparent plastic, which can be anywhere from brittle to flexible. Nitrocellulose (mainly $C_6H_7N_3O_{11}$) is made using either concentrated sulfuric/nitric acid or sulfuric acid/potassium nitrate. In general, cotton is used as the cellulose. The cellulose is added to the acid mix to nitrate. When used as a propellant or low-order explosive, it is known as guncotton (guncotton; dissolved at approximately 25 % in acetone, forms a lacquer used in preliminary stages of wood finishing to develop a hard finish with a deep luster. It is normally the first coat applied, sanded, and followed by other coatings that bond to it). Process uses the nitric acid to convert the cellulose into cellulose nitrate and water is shown:

$$3HNO_3 + C_6H_{10}O_5 \rightarrow C_6H_7(NO_2)_3O_5 + 3H_2O$$

The sulfuric acid is present as a catalyst to produce nitronium ion, NO_2^+. Nitrocellulose is widely used as support in diagnostic tests where antigen-antibody binding occur, e.g., pregnancy tests, U-Albumin tests and CRP.

Nitrocellulose has the following properties: Variable Molar mass, Appearance; It is a white, yellow or transparent plastic, Specific gravity of 1.41, It forms a hard but flexible film – ideal for a good surface finish, Is a highly flammable compound, dissolves readily in organic solvents, Flash point of 4.4 °C, and Melting point of 160-170 °C (ignites) (Urbanski, 1965).

0ther forms of nitrocellulose can be produce and perform different function as;

Propellant: Nitrocellulose is used primarily as a propellant as are most modern military low-order explosives. Propellants impart motion to something like a rocket or projectile.

Guncotton: This material was extremely flammable and therefore unsuitable for use in textiles, but it was useful as an explosive and it became known as guncotton. Guncotton was the precursor of nitrocellulose, or smokeless powder.

Gunpowder: To make nitrocellulose gunpowder, the nitrocellulose is dissolved in certain organic solvents such as an ether-ethanol mixture or acetone and it becomes a gelatinous mass. More modern solvents can also be used. When the solvents evaporate, a hard plastic material remains. This gelatinous blob is usually rolled into a sheet before it hardens. Afterwards, it is cut up into flakes of various sizes and shapes. The size and shape of the flakes controls the material's burning characteristics. The cutting is done on machines because the particles are tiny and it takes a great deal of cutting.

Nitrocellulose can also be produce depending on the source

1. Production of Nitrocellulose By Powerlab

(For curiosity purposes only, POWERLABS outlines the method used for making rocket-fuel and double base powder grade nitrocellulose.) The procedure is very similar to the one outlined by this project work, except it uses a slightly different nitrating mixture (http//www.powerlab.org).

2. Producing Cellulose Nitrate (From Andrew)

He used to make nitrocellulose, though. It was not guncotton grade, because he didn't have oleum (H_2SO_4 with dissolved SO_3); nevertheless it worked (http//www.skepticfiles.org).

3. Wolff Cellulosic's, a division of Bayer Material science.

Nitrocellulose is produced by causing cellulose to react with nitrating acid (a mixture of nitric acid and sulphuric acid). Following complex washing and stabilizing stages, damping agents (alcohols or water) or plasticizers are added to the nitrocellulose which is then marketed as Walsroder Nitrocellulose or Walsroder NC-Chips (www.azom.com).

4. Adam Hauwa, Federal Polytechnic Kaduna

Hauwa Adam uses Cotton, Sulphuric acid, Nitric acid, Acetone (NC lacquer) and distilled water in producing nitrocellulose with exception of saturated sodium bicarbonate solution that is used for neutralising cellulose nitrate first before using distilled water (Hauwa A., 2008).

5. **U.S. Pat. No. 3,284,253** describes a process for the production of nitrocellulose moistened with a non-solvent. The **disadvantage** of these know processes for the production of free-flowing nitrocelluose lie in the elaborate treatments of the nitrocellulose with the non-solvent, particularly the distillation step for removing the non-solvent used in the softening of the nitrocellulose. This process step can be avoided by the process according to the present invention (http//www.google.com).

In general, in this research work the nitrocellulose produced can be use in different ways: As a base material for coatings, Printing inks and in leather finishes – e.g. for shoes.

1.1 Aims and Objectives

This research work is aimed at producing nitrocellulose Resin from cotton (which forms a lacquer used in preliminary stages of wood finishing developing a hard finish with a deep luster, Printing inks and in leather finishes). This is a view of developing new product from locally available raw materials like cotton fibres, wood fibres etc using a process of nitration.

1.2 Scope

The scope of this research is based on the production of nitrocellulose resin from cotton.

1. To determine the physical and chemical properties of the products.
2. To compare the nitrocellulose produced with the available one in the market.
3. To convert cotton into a useful nitrocellulose product.

1.3 Limitations

The problem faced, was during the preparations of sulfuric acid and nitric acid, which causes damage to skin this is due the fact that sulfuric acid are potentially hazardous which cause tissue damage due to dehydration and particularly due to the heat liberated by the reaction.

1.4 Justification of the Work

Nitrocellulose is a product that has found many uses on everyday life which can be anywhere from brittle to flexible. It is less capital intensive with it major raw material (cellulose) readily available with many socio-economic and environment benefits;

1. As a base material for coatings.
2. As leather finishes.
3. It can be made into many different forms that maintain their shape Production of organic fertilizer.

CHAPTER TWO

2.0 BACKGROUND THEORY

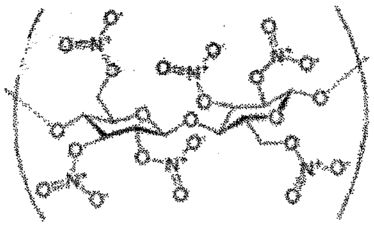
Nitrocellulose (mainly $C_6H_7N_3O_{11}$) was used as the first flexible film base, beginning with Eastman Kodak products in August, 1889. Camphor is used as plasticizer for nitrocellulose film. It was used until 1933 for X-ray films (where its flammability hazard was most acute) and for motion picture film until 1951. It was replaced by safety film with an acetate base. It was discovered that nitrocellulose gradually decomposes, releasing nitric acid, further catalyzing the decomposition (eventually into a still-flammable powder or goo). Decades later storage at low temperatures was discovered as a means of delaying these reactions indefinitely. It is estimated that the greate majority of films produced during the early twentieth century were lost forever either through this accelerating, self-catalyzed disintegration or through studio warehouse fires.

However, Christian Friedrich Schönbein, a German-Swiss chemist, discovered a more practical solution around 1846. As he was working in the kitchen of his home in Basle, he spilled a bottle of concentrated nitric acid on the kitchen table. He reached for the nearest cloth, a cotton apron, and wiped it up. He hung the apron on the stove door to dry, and, as soon as it was dry, there was a flash as the apron exploded. His preparation method was the first to be widely imitated — one part of fine cotton wool to be immersed in fifteen parts of an equal blend of sulfuric and nitric acids. After two minutes, the cotton was removed and washed in cold water to set the esterification level and remove all acid residues. It was then slowly dried at a temperature below 100 °C.

The process uses the nitric acid to convert the cellulose into cellulose nitrate and water:

$$3HNO_3 + C_6H_{10}O_5 \rightarrow C_6H_7(NO_2)_3O_5 + 3H_2O$$

The sulfuric acid is present as a catalyst to produce nitronium ion, NO_2^+. The reaction is first order and proceeds via electrophilic substitution at the C-OH centers of the cellulose. Depending on the manufacturing process, nitrocellulose is esterified to varying degrees.



2-dimensional nitrocellulose structural formular

2.1 Applications of Nitrocellulose

2.1.1 Propellant

Nitrocellulose is used primarily as a propellant as are most modern military low-order explosives. Propellants impart motion to something like a rocket or projectile. They are classified as single-base, double-base and composites. Single-base propellants are the simple forms of nitrocellulose powders. Double-based propellants are nitrocellulose powders that have nitroglycerin added to them thus making them more powerful. Composite propellants are mixtures of fuels and oxidizers that are mostly not nitrocellulose and nitroglycerin.

2.1.2 Nitrocellulose Plastics

Nitrocellulose had many properties that made it an important material apart from its use as a propellant. Since it forms a plastic material when dissolved in organic solvents like ether-alcohol or acetone, it can be made into many different forms that maintain their shape when the solvents evaporate. It can also be hot-formed and will retain its shape when cooled.

2.1.3 Coatings

As a base material for coatings, nitrocellulose will continue to be indispensable. Nitrocellulose lacquers and varnishes are particularly valuable for accentuating wood grain.

2.1.4 Printing Inks

Printing inks containing Nitrocellulose dry very quickly. Another very important advantage, particularly with food packaging, is that the solvents evaporate completely.

2.1.5 Leather Finishes

In leather finishes – e.g. for shoes – the high flexibility of nitrocellulose is a significant asset.

2.2 Properties of Nitrocellulose

2.2.1 Physical Properties

1. Molar mass: Variable
2. Relative density (water=1):1.66
3. Appearance: It is a white, yellow or transparent plastic
4. Specific gravity: 1.41
5. It forms a hard but flexible film – ideal for a good surface finish.

2.2.2 Chemical Properties

1. Is a highly flammable compound
2. It dissolves readily in organic solvents
3. Explosive and can deflagrate or even detonate violently on shock, friction, or spark when dry
4. Flash point: 4.4 °C
5. Melting point: 160-170 °C (ignites) (Urbanski, Tadeusz, 1965).

2.3 Resin

Resin is a hydrocarbon secretion of many plants, particularly coniferous trees. It is valued for its chemical constituents and uses, such as varnishes and adhesives, as an important source of raw materials for organic synthesis, or for incense and perfume. Fossilized resins are the source of amber. Resins are also a material in nail polish.

The term is also used for synthetic substances of similar properties. Resins have a very long history and are mentioned by both ancient Greek Theophrastus and ancient Roman Pliny the Elder, especially as the forms known as frankincense and myrrh. They were highly prized substances used for many purposes, especially perfumery and as incense in religious rites.

2.3.1 Chemistry of Resin

The resin produced by most plants is a viscous liquid, composed mainly of volatile fluid terpenes, with lesser components of dissolved non-volatile solids which make resin thick and sticky. The most common terpenes in resin are the bicyclic terpenes alpha-pinene, beta-pinene, delta-3 carene and sabinene, the monocyclic terpenes limonene and terpinolene, and smaller amounts of the tricyclic sesquiterpenes, longifolene, caryophyllene and delta-cadinene. Some resins also contain a high proportion of resin acids. The individual components of resin can be separated by fractional distillation

A few plants produce resins with different compositions, most notably Jeffrey Pine and Gray Pine, the volatile components of which are largely pure n-heptane with little or no terpenes. The exceptional purity of the n-heptane distilled from Jeffrey Pine resin, unmixed with other isomers of heptane, led to its being used as the defining zero point on the octane rating scale of petrol quality. Because heptane is highly flammable, distillation of resins containing it is very dangerous. Some resin distilleries in California exploded because they mistook Jeffrey Pine for the similar but terpene-producing Ponderosa Pine. At the time the two pines were considered to be the same species of pine; they were only classified as separate species in 1853.

Some resins when soft are known as 'oleo-resins', and when containing benzoic acid or cinnamic acid they are called balsams. Other resinous products in their natural condition are a mix with gum or mucilaginous substances and known as gum resins. Many compound resins have distinct and characteristic odors, from their admixture with essential oils.

Certain resins are obtained in a fossilized condition, amber being the most notable instance of this class; African copal and the kauri gum of New Zealand are also procured in a semi-fossil condition. (http://wikipedia.org)

2.3.2 Synthetic Resins

Synthetic resins are materials with similar properties to natural resins—viscous liquids capable of hardening. They are typically manufactured by esterification or soaping of organic compounds. The classic variety is epoxy resin, manufactured through polymerization-polyaddition or polycondensation reactions, used as a thermoset polymer for adhesives and composites. One more category, which constitutes 75% of resins used, is unsaturated polyester resin. Ion exchange resin is another important class with application in water purification and catalysis of organic reactions (Urbanski, Tadeusz, 1965).

2.3.3 Uses of Resin

1. The hard transparent resins, such as the copals, dammars, mastic and sandarac, are principally used for varnishes and cement.
2. The softer odoriferous oleo-resins and gum resins containing essential oils are more largely used for therapeutic purposes and incense.
3. Resin in the form of rosin is used for the upkeep of bows for stringed instruments because of its quality for adding friction to the hair. Ballet dancers may apply crushed rosin to their shoes to increase grip on a slippery floor.
4. Resin has also been used as a medium for sculpture by artists such as Eva Hesse, and in other types of artwork.
5. Resin is also used in some skateboard decks. It makes the skateboard more durable, making it less likely to get pressure-related cracks, chipping, or breaking in half.

2.4 Cotton

Cotton is a soft, staple fibre that grows in a form known as a boll around the seeds of the cotton plant, a shrub native to tropical and subtropical regions around the world, including the Americas, India and Africa. The fibre most often is spun into yarn or thread and used to make a soft, breathable textile, which is the most widely, used natural-fibre cloth in clothing today. Cotton today is the most used textile fibre in the world. Its current market share is 56 percent for all fibres used for apparel and home furnishings.

Cotton was cultivated by the inhabitants of the Indus Valley Civilization by the 5th millennium BC - 4th millennium BC. The Indus cotton industry was well developed and some methods used in cotton spinning and fabrication continued to be used until the modern Industrialization of India. Cotton remained a key crop in the southern economy after emancipation and the end of the civil war in 1865. Across the South, sharecropping evolved, in which free black farmers worked on white-owned cotton plantations in return for a share of the profits. Cotton plantations required vast labor forces to hand-pick cotton, and it was not until the 1950s that reliable harvesting machinery was introduced into the South (prior to this, cotton-harvesting machinery had been too clumsy to pick cotton without shredding the fibres). During the early twentieth century, employment in the cotton industry fell as machines began to replace labourers, and as the South's rural labour force dwindled during the First and Second World Wars. Today, cotton remains a major export of the southern United States, and a majority of the world's annual cotton crop is of the long-staple American variety. Successful cultivation of cotton requires a long frost-free period, plenty of sunshine, and a moderate rainfall, usually from 600 to 1200 mm (24 to 48 inches). Soils usually need to be fairly heavy, although the level of nutrients does not need to be exceptional (Matthew's, 1954).

2.4.1 Uses of Cotton

1. Cotton is used to make a number of textile products. These include:

- Terrycloth
- Cotton used to make highly absorbent bath towels and robes; denim
- Used to make blue jeans; chambray, popularly used in the manufacture of blue work shirts (from which we get the term "blue-collar"); and corduroy, seersucker, and cotton twill. Socks, underwear, and most T-shirts are made from cotton. Bed sheets often are made from cotton.

2. Cotton also is used to make yarn used in crochet and knitting.
3. It can either be used in knitted or woven fabrics, as it can be blended with elastine to make a stretchier thread for knitted fabrics, and things such as stretch jeans.

2.4.2 Characteristics of Cotton

Cotton, as a natural cellulosic fibre, has a lot of characteristics, such as;

- Comfortable Soft hand
- Good absorbency
- Color retention
- Prints well
- Machine-washable
- Dry-cleanable
- Good strength
- Drapes well
- Easy to handle and sew

2.4.3 Raw cotton components:

• 80-90 %	Cellulose
• 6-8 %	Water

0.5 – 1 %	Waxes and fats
0 - 1.5 %	Proteins
4 – 6 %	Hemicelluloses and pectin's
1 - 1.8 %	Ash

2.5 Properties of Cotton

2.5.1 Physical Properties of Cotton

Fiber Length

Fiber length is described as "the average length of the longer one-half of the fibers (upper half mean length)" This measure is taken by scanning a "beard" of parallel fibers through a sensing region. The beard is formed from the fibres taken from the sample, clasped in a holding clamp and combed to align the fibers. Typical lengths of Upland cottons might range from 0.79 to 1.36 in.

Length Uniformity

Length uniformity or uniformity ratio is determined as " a ratio between the mean length and the upper half mean length of the fibers and is expressed as a percentage. Typical comparisons are illustrated below.

LENGTH UNIFORMITY	UNIFORMITY INDEX [%]	
Very High	>85	
High	83-85	
Intermediate	80-82	
Low	77-79	
Very Low	<77	(Matthew's, 1954)

2.5.2 Chemical Properties of Cotton

- Cotton can degrade by exposure to visible and ultraviolet light, especially in the presence of high temperatures around 250~397 ^{O}C and humidity.
- Cotton fibers show double refraction when observed in polarized light.

  Cotton is attacked by hot dilute or cold concentrated acid solutions (Lawrence H. Shaw, 1988)

2.6 Cotton Linter

Linters are used for absorbent cotton swabs, and for manufacture of many cellulose products such as rayon, plastics, lacquers, and smokeless powder for munitions. The hulls, or husks, are used as feed for cattle.

Cotton linters are fine, silky fibers which adhere to the seeds of the cotton plant after ginning. These curly fibers typically are less than 1/8 in (3 mm) long. The term also may apply to the longer textile fiber staple lint as well as the shorter fuzzy fibres from some upland species. Linters are traditionally used in the manufacture of paper and as a raw material in the manufacture of cellulose.

2.7 Cotton Fiber

Cotton is a soft, staple fibre that grows in a form known as a boll around the seeds of the cotton plant, a shrub native to tropical and subtropical regions around the world, including the Americas, India and Africa. The fibre most often is spun into yarn or thread and used to make a soft, breathable textile, which is the most widely, used natural-fibre cloth in clothing today.

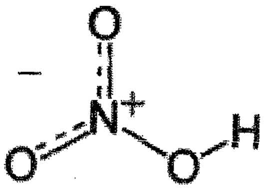
Cotton dries out, becomes hard and brittle and loses all elasticity at temperatures above 25 °C (77 °F). Extended exposure to light causes similar problems. A temperature range of 25 °C (77 °F) to 35 °C (95 °F) is the optimal range for mold development. At temperatures below 0°C (32 °F), rotting of wet cotton stops. Damaged cotton is sometimes stored at these temperatures to prevent further deterioration.

2.7.1 Properties of Cotton Fibres

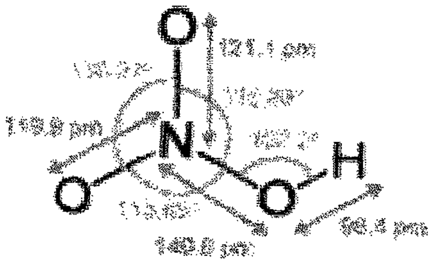
Fibres Property	***Evaluation***
Shape	Fairly uniform in width, 12-20 micrometers; length varies from 1 cm to 6 cm (½ to 2½ inches); typical length is 2.2 cm to 3.3 cm (⅞ to 1¼ inches).
Luster	high
Density	1.54-1.56 g/cm^3
Dimensional stability	good
Resistance to:	
Acids	damage, weaken fibers
Alkali	resistant; no harmful effects
Sunlight	Prolonged exposure weakens fibers.
Microorganisms	Mildew and rot-producing bacteria damage fibres.
Insects	Silverfish damage fibers.
Thermal reactions:	
To heat	Decomposes after prolonged exposure to temperatures of 150°C or over.
To flame	Burns readily.

2.8 Nitric Acid

Nitric acid (HNO_3), also known as aqua Fortis and spirit of nitre, is a highly corrosive and toxic strong acid that can cause severe burns. Colourless when pure, older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. If the solution contains more than 86 % nitric acid, it is referred to as fuming nitric acid. Fuming nitric acid is characterized as white fuming nitric acid and red fuming nitric acid, depending on the amount of nitrogen dioxide present. Below is the Nitric Acid structure



Nitric Acid (IUPAC name)



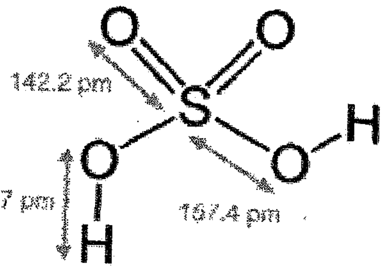
2.8.1 Properties of Nitric Acid

Molecular formula	HNO_3
Molar mass	63.012 g/mol
Appearance	Clear, colorless liquid
Density	1.5129 g/cm3
Melting point	-42 °C, 231 K, -44 °F
Boiling point	bp of pure acid. 68 % solution boils at 120.5 °C
Solubility in water	miscible
Acidity (pKa)	-1.4
Flash point	Non-flammable

(Urbanski, Tadeusz, 1965)

2.9 Sulfuric Acid

Sulfuric (or sulphuric) acid, H_2SO_4, is a strong mineral acid. It is soluble in water at all concentrations. Sulfuric acid has many applications, and is one of the top products of the chemical industry. World production in 2001 was 165 million tonnes, with an approximate value of US$8 billion. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis. Molecular structure sulphuric acid is shown below



2.9.1 Occurrence

Pure (undiluted) sulfuric acid is not encountered naturally on Earth, due to sulfuric acid's great affinity for water. Apart from that, sulfuric acid is a constituent of acid rain, which is formed by atmospheric oxidation of sulfur dioxide in the presence of water i.e., oxidation of sulfurous acid. Sulfur dioxide is the main byproduct produced when sulfur-containing fuels such as coal or oil are burned.

Sulfuric acid is formed naturally by the oxidation of sulfide minerals, such as iron sulfide. The resulting water can be highly acidic and is called acid mine drainage (AMD) or acid rock drainage (ARD). This acidic water is capable of dissolving metals present in sulfide ores, which results in brightly-colored, toxic streams. The oxidation of iron sulfide pyrite by molecular oxygen produces iron (II), or Fe2+:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ Fe_2^+ + 4\ SO4_2^- + 4\ H^+.$$

The Fe_2^+ can be further oxidized to Fe_3^+, according to:

$$4\ Fe_2^+ + O_2 + 4\ H^+ \rightarrow 4\ Fe_3^+ + 2\ H_2O,$$

And the Fe_3^+ produced can be precipitated as the hydroxide or hydrous oxide. The equation for the formation of the hydroxide is

$$Fe_3^+ + 3\ H_2O \rightarrow Fe\ (OH)_3 + 3\ H^+.$$

The iron (III) ion ("ferric iron", in casual nomenclature) can also oxidize pyrite. When iron (III) oxidation of pyrite occurs, the process can become rapid. pH values below zero have been measured in ARD produced by this process.

2.9.2 Properties of Sulfuric Acid

Molecular formula	H_2SO_4
Molar mass	98.08 g/mol
Appearance	clear, colorless, odorless liquid
Density	1.84 g/cm^3, liquid
Melting point	10 °C, 283 K, 50 °F
Boiling point	290 °C, 563 K, 554 °F
Solubility in water	miscible
Acidity (pKa)	−3
Viscosity	26.7 cP (20 °C)
EU classification	Corrosive (C)
Flash point	Non-flammable

2.9.3 Uses of Sulfuric Acid

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength.

1. The major use (60 % of total production worldwide) for sulfuric acid is in the "wet method" for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as trisodium phosphate for detergents.

2. Sulfuric acid is used in large quantities by the iron and steel making industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white-goods industry.
3. Used acid is often recycled using a Spent Acid Regeneration (SAR) plant. These plants combust spent acid with natural gas, refinery gas, fuel oil or other fuel sources. This combustion process produces gaseous sulfur dioxide (SO_2) and sulfur trioxide (SO_3) which are then used to manufacture "new" sulfuric acid.
4. Another important use for sulfuric acid is for the manufacture of aluminum sulfate, also known as paper maker's alum. This can react with small amounts of soap on paper pulp fibers to give gelatinous aluminum carboxylates, which help to coagulate the pulp fibers into a hard paper surface.
5. It is also used for making aluminum hydroxide, which is used at water treatment plants to filter out impurities, as well as to improve the taste of the water. Aluminum sulfate is made by reacting bauxite with sulfuric acid:

   $Al_2O_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2O$. **(Edward M. Jones, 1950)** don't Understand

2.9.4 Laboratory Hazards

The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. Hence burns from sulfuric acid are potentially more serious than those of comparable strong acids (e.g. hydrochloric acid), as there is additional tissue damage due to dehydration and particularly due to the heat liberated by the reaction with water; i.e. secondary thermal damage. The danger is obviously greater with more concentrated preparations of sulfuric acid, but it should be remembered that even the normal laboratory "dilute" grade (approx. 1 M, 10%) will char paper by dehydration if left in contact for a sufficient time. Solutions equal to or stronger than 1.5 M should be labeled CORROSIVE, while solutions greater than 0.5 M but less than 1.5 M should be labeled IRRITANT.

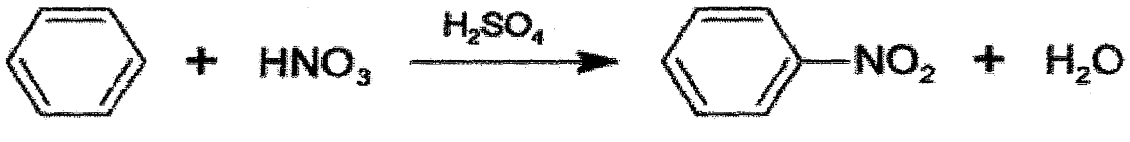
Fuming sulfuric acid (oleum) is not recommended for use in schools due to it being quite hazardous

2.10 Nitration

Nitration is a general chemical process for the introduction of a nitro group into a chemical compound. Examples of nitrations are the conversion of glycerin to nitroglycerin and the conversion of toluene to trinitrotoluene. Both of these conversions use nitric acid and sulfuric acid.

Aromatic Nitration

In aromatic nitration, aromatic organic compounds are nitrated via an electrophilic aromatic substitution mechanism involving the attack of the electron-rich benzene ring by the nitronium ion.



Aromatic nitro compounds are important intermediates to anilines by action of a reducing agent. Benzene is nitrated by refluxing with concentrated sulphuric acid and concentrated nitric acid at 50°C.The sulphuric acid is regenerated and hence acts as a catalyst. It also absorbs water.

2.11 Acetone

Acetone is the organic compound with the formula $(CH_3)_2CO_{(l)}$. This colorless, mobile, flammable liquid is the simplest example of the ketones. Owing to the fact that acetone is miscible with water, and virtually all organic solvents, it serves as an important solvent in its own right, typically the solvent of choice for cleaning purposes in the laboratory. Familiar household uses of acetone are as the active ingredient in nail polish remover and as paint thinner and sanitary cleaner/ nail polish remover base. It is a common building block in organic chemistry. In addition to being manufactured, acetone also occurs naturally, even being biosynthesized in small amounts in the human body. Acetone evaporates rapidly, even from water and soil. **(Lozano, 1992)**

2.12 Method of Producing Nitrocellulose by Some Sources

Production of Nitrocellulose by Powerlab

(For curiosity purposes only, POWERLABS outlines the method used for making rocket-fuel and double base powder grade nitrocellulose).

The procedure is very similar to the one outlined by this project work, except it uses a slightly different nitrating mixture. The proportions are now 35 % / 65 % (by volume) for HNO_3 / H_2SO_4, assuming that the acid concentrations used were the same as the ones used in this project work. 5 parts of acid are used for every part of dry cellulose (per weight). An alternate nitrating mixture is made by adding 1gram of finely powdered Potassium or Sodium Nitrate (KNO_3/$NaNo_3$) for every 3.325 g (3.819 ml) of cold concentrated Sulphuric Acid (H_2SO_4), and then adds cotton to this nitrating mixture when the temperature has stabilized.

This particular procedure because it is hazardous (there is a lot of heat involved in the formation of nitric acid by removal of nitrate from the potassium ion) and can cause sputtering as well as releasing toxic fumes. Plus resultant mixture is not only nitric and sulphuric acids, but also includes potassium or sodium sulphate, which will have a negative effect on the quality of the final product.

Complete nitration takes about 10 minutes at room temperature. On a small scale not enough heat is evolved to justify an ice bath, which would only slow the process down. The mixture with a greater sulphuric acid content is able to impart more nitrate ions to the cellulose, causing it to have a much higher nitrate (nitrogen and oxygen) content. The procedure is still reasonably safe to perform from a stability point of view (meaning that it is virtually impossible for the nitrocellulose to form upon formation), but now the resultant product (when dry) burns a lot faster, hotter, and releases much more energy than the trinitrate above. It is, in fact, one of the most energetic deflagrants known, capable of DDT (Deflagration - Detonation Transition) with 123-147 % the explosive strength of TNT when detonated at 7300 meters per second (Nitrocellulose (13.35 % N) max density 1.2 g/cc).

NOTE: It is very important to thoroughly neutralize the nitrocellulose by boiling it in $NaHCO_3$ and in distilled water several times until it tests neutral. It is also recommendable to add 0.5-1 % of Urea or diphenylamine in fine powder form to neutralize any remaining nitrogen oxides that could become acidic in moisture and causing accidental ignition of the product.

This product can be stored safely under water or dissolved in acetone (NC Lacquer). The nitrocellulose produced by this method is EXPLOSIVE and can deflagrate or even detonate violently on shock, friction, or spark when dry. These procedures are not to be attempted, and are outlined here only for informational purposes. (http//www.powerlab.org)

Producing Cellulose Nitrate *(From Andrew)*

He used to make nitrocellulose, though. It was not guncotton grade, because he didn't have oleum (H_2SO_4 with dissolved SO_3); nevertheless it worked.

At first he got H_2SO_4 from a shop in downtown. Not only was the acid concentrated, cheap and plentiful, it came with enough carbonate to clean up. He add KNO_3 and a little water (OK, I'd add the acid to the water - but there was so little Water, what was added to what made little difference. It spattered

Concentrated H_2SO_4 either way). Later on, when he could purchase the acids, he used 3 parts H_2SO_4 to 1 part HNO_3. For cotton, he used cotton wool or cotton cloth. Runaway nitration was commonplace, but it is usually not so disasterous with nitrocellulose as it is with nitroglycerine. For some reason, he tried washing the cotton cloth in a solution of lye, and rinsing it well in distilled water. He let the cloth dry and then nitrated it. When the product was nitrated, he never got a runaway reaction. BTW, water quenched the runaway reaction of cellulose.

The product was washed thoroughly and allowed to dry. It dissolved (or turned into mush) in acetone. It dissolved in alcohol/ether.

WARNINGS: All usual warnings regarding strong acids apply. H_2SO_4 likes to spatter. When it falls on the skin, it destroys tissue - often painfully. It dissolves all manner of clothing. Nitric acid also destroys skin, turning it bright yellow in the Process. (http//www.skepticfiles.org)

Wolff Cellulosic's, A Division of Bayer Material Science.

Nitrocellulose is produced by causing cellulose to react with nitrating acid (a mixture of nitric acid and sulphuric acid). Following complex washing and stabilizing stages, damping agents (alcohols or water) or plasticizers are added to the nitrocellulose which is then marketed as Walsroder Nitrocellulose or Walsroder NC-Chips. The raw material used for producing Walsroder Nitrocellulose and Walsroder NC-Chips is carefully selected and well-characterized types of cellulose, the exact specifications having been agreed with the cellulose suppliers.

The cellulose is caused to react with the nitrating acid (a mixture of nitric acid and sulfuric acid) in the nitrating process. A new nitrating plant came on stream at Wolff Cellulosics in 1996. It is a state-of-the-art production unit incorporating 125 years of nitrocellulose manufacturing experience.

After nitration, centrifuges separate the nitrocellulose from the spent nitrating acid used in excess quantities. This spent nitrating acid is separated into nitric acid, sulfuric acid and water, and completely recycled back into the process.

The next stage is the pre-stabilization stage where the nitrocellulose is washed with water, thus separating off any acid left on the fibres. Next, the viscosity of the nitrocellulose is adjusted by pressure boiling (heating under pressure to temperatures above 100 °C).

This is followed by the post-stabilization stage where the nitrocellulose is washed with water and heated to temperatures below 100 °C. The water is subsequently separated off to leave a water content of 35 %. This water-wet nitrocellulose can then be packaged. To produce alcohol-damped Walsroder Nitrocellulose, the water is replaced with the appropriate damping alcohol. To produce Walsroder NC-Chips, the appropriate plasticizer is added to water-wet nitrocellulose which is then dried.

In the course of the entire production process all relevant properties of the nitrocellulose and of the process are constantly monitored to ensure the consistent high quality of Walsroder Nitrocellulose and Walsroder NC-Chips **(www.azom.com).**

U.S. Pat. No. 3,284,253

U.S. Pat. No. 3,284,253 describes a process for the production of nitrocellulose moistened with a non-solvent. In this process, the nitrocellulose is first softened by the addition of an amount of an organic solvent to an aqueous nitro-cellulose suspension such that the nitrocellulose structure disappears, and then processed into a granulate, the organic solvent being distilled off and the remaining excess water separated off. A volatile non-solvent, preferably toluene, is added to this moist nitrocellulose and the water azeotrope is distilled off so that a free-flowing nitrocellulose moistened with toluene is ultimately obtained.

The **disadvantage** of these known processes for the production of free-flowing nitrocelluose lie in the elaborate treatments of the nitrocellulose with the non-solvent, particularly the distillation step for removing the non-solvent used in the softening of the nitrocellulose. This process step can be avoided by the process according to the present invention. The process according to the invention is preferably carried out by briefly treating the alcohol- or water-moist nitrocellulose while stirring with the solvent mixture until the nitrocellulose fibers have softened and dissolved (which takes from 1 to 10 minutes and preferably from 2 to 5 minutes), switching off the stirrer and then leaving the mixture standing until a two-phase mixture is formed, separating off the liquid phase, spinning the nitrocellulose-containing phase into filaments in a screw extruder and granulating the resulting filaments. Normally, these granulates contain some residues of the solvent which was used for softening the nitrocellulose. In order to completely remove any solvent residues which may be present, the granulate may be extracted with the moistening agent which is also used for storage of the nitrocellulose.

The free-flowing nitrocellulose produced in accordance with the invention is distinguished by its high powder density and very low dust content which makes it safer to store and transport. The nitrocellulose thus produced treated with moistening agent may be used for the production of any paints and lacquers containing nitrocellulose (http//www.google.com).

2.13 Factorial Design

It is one of the tools that researchers can use to design experiments. An experiment using factorial design allows one to examine simultaneously the effects of multiple independent variables and their degree of interaction. In statistics, a full factorial experiment is an experiment whose design consists of two or more factors, each with discrete possible values or "levels", and whose experimental units take on all possible combinations of these levels across all such factors. A full factorial design may also be called a fully-crossed design. Such an experiment allows studying the effect of each factor on the response variable, as well as the effects of interactions between factors on the response variable **(www.socialresearchmethods.net)**.

For the vast majority of factorial experiments, each factor has only two levels. For example, with two factors each taking two levels, a factorial experiment would have four treatment combinations in total, and is usually called a 2×2 factorial design. If the number of combinations in a full factorial design is too high to be logistically feasible, a fractional factorial design may be done, in which some of the possible combinations (usually at least half) are omitted. Example

Table2.0: 2×2 factorial experiment

S/No	A	B
1	-	-
2	+	-
3	-	+
4	+	+

For more than two factors, a 2^k factorial experiment can be recursively designed from a 2^{k-1} factorial experiment by replicating the 2^{k-1} experiment, assigning the first replicate to the first (or low) level of the new factor, and the second replicate to the second (or high) level. This framework can be generalized to, e.g., designing three replicates for three level factors, etc.

Table 2.1: 2×3 factorial experiment

RUN	A	B	C
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

(www.socialresearchmethods.net)

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 Materials

In the course of this project work the following material were used

Table 3.0: The list of material used

REAGENT	**COMMENT**
Pure Cotton	90 % Cellulose $C_6H_{10}O_{5(s)}$
Sulphuric acid ($H_2So_{4(l)}$)	98 % Concentrated
Nitric acid ($HNO_{3(aq)}$)	70 % Concentrated
Acetone (NC lacquer) ($(CH_3)_2CO_{(l)}$)	
Distilled water (l)	
Sodium bicarbonate solution ($NaHCO_{3(S)}$)	

Table 3.1: List of apparatus used

Apparatus	**Number needed**	**comment**
Measuring cylinder	2	250 ml Pyrex glass and 100 ml
Beaker	5	4 × 250 ml Pyrex glass and 500 ml Pyrex glass
Glass stirrer	2	
Weighing balance	1	
0ven	1	
Litmus paper	10 piece	

3.2 Methodology

Step One

The raw-material used for the production of nitrocellulose includes sulphuric acid, nitric acid, acetone, distilled water, saturated sodium bicarbonate solution and cotton.

Step Two

The proportion by volume of nitric acid and sulphuric acid were formulated by *2×3* factorial design, an experiment using factorial design allows one to examine simultaneously the effects of multiple independent variables and their degree of interaction. In statistics, a full factorial experiment is an experiment whose design consists of two or more factors, each with discrete possible values or "levels", and whose experimental units take on all possible combinations of these levels across all such factors. Such an experiment allows studying the effect of each factor on the response variable, as well as the effects of interactions between factors on the response variable (www.socailresearchmethods.net).

Step Three

When the temperature of the mixture has stabilized the cotton was immerse and mixed together for nitration. Complete nitration take about 5 - 10 minutes at a room temperature.

Step Four

The resultant product when dry burns a lot faster, hotter and releases much more energy. It is very important to thoroughly neutralise the product by washing it once in saturated sodium bicarbonate solution and 2 times in distilled water until it tests neutral. It was then allowed to thoroughly dry and dissolved in acetone. The acetone was then allowed to vaporize until a concentrated syrup-like nitrocellulose lacquer formed. This product can be stored safely under water.

3.3 Experimental Procedure

In order to produce nitrocellulose from cotton the following details procedure were carried out.

The volumes (according to the two by three factorial designs) of concentrated sulphuric acid and concentrated nitric acid were measured with the use of measuring cylinder and mixed together in a beaker and were allowed to stabilize. **2.0**gram of cotton was weighed with the use of weighing balance and was immersed in a beaker containing the mixture and stir with a glass stirrer which was then allowed to nitrate for about 5 – 10 minutes at room temperature while stirring. The product obtained after nitration was removed from the mixture and then washed once with saturated sodium bicarbonate solution and 2 times in distilled water, until the leftover water tested neutral, to ascertain if there is no more trace of acid. The product was tested with a litmus paper when it turn litmus blue to red it means there are still some traces of acid in the cotton, it then rewash with distilled water until it tests neutral. The product is then dried at temperature of about 75°c, after it been dried it was then dissolved in acetone (NC lacquer). The acetone was then allowed to vaporize until a concentrated syrup-like nitrocellulose lacquer formed.

3.4 Two by three (2×3) factorial design

During the experiment using two by three (2×3) factorial designs, two parameters were considered to be changing, the parameters are:

1. Volume of sulphuric acid
2. Volume of nitric acid

Table 3.2: factorial design using 2×3 factorial design

No of experiment	***Parameters to be consider***		
	Volume of H_2SO_4 (ml)	***Volume of HNO_3 (ml)***	***Volume of $((CH_3)_2CO_{(l)})$ (ml)***
1	75	75	75
2	70	70	70
3	60	70	70
4	50	70	70
5	40	70	70
6	70	60	70
7	70	50	70
8	70	40	70

Weight of the cotton = 2.0 gram per experiment

Volume of distilled water = 100 ml per experiment

Volume of sodium bicarbonate solution = 50 ml per experiment

Experiment one is the reference work consider for the practical.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

The experiment was carried out according to the two by three **(2×3)** factorial design methods and the results are;

Weight of 250 ml beaker used (Pyrex) = 97.4 g

Weight of 500 ml beaker used (Pyrex) = 160.49 g

Sodium bicarbonate solution prepared = 30 g of sodium bicarbonate was dissolved in 300 ml of distilled water.

- **Experiment 1:**

  Nitration time = 5 minutes

  Appearance of the product: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 15 ml

- **Experiment 2:**

  Nitration time = 6 minutes

  Appearance of the production: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 15 ml

- **Experiment 3:**

  Nitration time = 6 minutes

  Appearance of the product: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 10 ml

- **Experiment 4:**

  Nitration time = 8 minutes

  Appearance of the product: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 15 ml

- **Experiment 5:**

  Nitration time = 5 minutes

  Appearance of the product: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 10 ml

- **Experiment 6:**

  Nitration time = 5 minutes

  Appearance of the product: Yellowish white product

  Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

  Volume of product obtained = 10 ml

- **Experiment 7:**

Nitration time = 5 minutes

Appearance of the product: Yellowish white product

Flammability: It burns all at once, with a fast bright flame and it does not produce any smoke.

Volume of product obtained = 15 ml

Table 4.0: summary of the results

S/No.	Volume of H_2SO_4 (ml)	Volume of HNO_3 (ml)	Nitration time (minutes)	Volume of product (ml)	appearance of product
1	70	70	5.0	15	yellowish white product
2	60	70	6.0	15	yellowish white product
3	50	70	6.0	15	yellowish white product
4	40	70	8.0	15	yellowish white product
5	70	60	5.0	15	yellowish white product
6	70	50	5.0	15	yellowish white product
7	70	40	5.0	15	yellowish white product
Total	430	430	40	105	yellowish white product

4.2 DISCUSSION OF RESULTS

In this research work of the production of nitrocellulose resin, the result was achieved by treating the cellulose (cotton) with the mixture of sulphuric acid and nitric acid by volume. The reactants were allowed to nitrate for about 5 – 10 min, the resulting product is yellow wish in colour (the yellow colour is due to carbon in the nitrocellulose molecule). The mixture with a greater sulphuric acid content is able to impact more nitrate ions to the cellulose, causing it to have much higher nitrate (nitrogen and oxygen) content. Therefore sulphuric acid is present as a catalyst during the reaction between the cellulose ($C_6H_{10}O_5$) feedstock and nitric acid (*HNO_3*). The sulphuric acid replaced the hydroxyl radicals in the cellulose structure with nitrate radicals. However, nitrocellulose and water was formed as shown

$$3HNO_3 + C_6H_{10}O_5 \rightarrow C_6H_7(NO_2)_3O_5 + 3H_2O$$

When nitrocellulose was burns, it burn all at once, with a fast bright flame yellow colour and no smoke was produced.

From the experiment carried out and the results obtained, it clearly showed that the more concentration of sulphuric acid present the faster the reaction and the better the yield of the product (nitrocellulose). The yield of the product also depend on the nitric acid since it gives out the nitrate radicals to the cellulose by replacing the hydroxyl radicals, considering this experiment all the volume of nitric acid used has the ability of substituting it nitrate radicals for a hydroxyl radical from the cellulose. From a view of an observation on this experiment it shows that the absent of sulphuric acid can produce nitrocellulose but not of good yield, but the absent of nitric acid can never yield nitrocellulose since it serve as one of the major constituent in the production. Considering acetone, what matters was the enough quantity of acetone that can be used to the nitrocellulose produced to form a lacquer product.

From the literature and comparison with standard, it can be clearly concluded that all the experiment are capable to yield the required product (nitrocellulose) within standard.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, this research project was made to be compared and analyse the produced nitrocellulose with the standard one. And the result obtained shows that there was no much deviation from the standard one .In this research work it can be seen that cellulose (cotton) and the mixture of sulphuric and nitric acid can be used to produce nitrocellulose resin (as a major constituent).

5.2 Recommendation

The finding of this research work recommend that nitrocellulose can be produced from Cellulose (cotton) further research should also focus on cellulose like wood pulp. Therefore I recommend that wood pulp should be tried so as to compare the quality of the product obtained.

REFERENCE

Edward M. Jones, (Nov 1950) "Chamber Process Manufacture of Sulfuric Acid," Industrial and Engineering Chemistry, Vol 42, No. 11, pp 2208-10

George t. Austin, (1984) Shrives chemical process industries fifth edition, McGraw hill international edition, Singapore, pp 155-177

http://www.sciencenews.org

http://www.powerlabs.org

http://www. wikipedia.org

Lozano, B. Yip and R. K. Hanson (1992). "Acetone: a tracer for concentration measurements in gaseous flows by planar laser-induced fluorescence".pp 96-100

Kilner E, Samuel D.N.,(1960). Applied organic chemistry second edition, Mac Donald and Evans limited, London, page.36-39

Kirk Othermer (1969) Encyclopaedia of chemical technology 2nd edition inter-science publishers. A division of John Wiley and Sons Inc. New York Vol.4, pp 593-637.

Lawrence H. Shaw (May 12, 1998) "Cotton's Importance in the Textile Industry", Symposium, Lima, Peru, pp 45-99

Matthew's (1954) "Textile Fibers, Their Physical, Microscopic and Chemical Properties", edited by Herbert R. Mauersberger, 6th edition, pp 67-77.

Urbanski, Tadeusz (1965) Chemistry and Technology of Explosives, Pergamon Press, Oxford, Vol 1, pp 20-21, 85-86.