RELATION OF COTTON TO LACQUERS†

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In developing the relation of cotton to lacquers, it is of first importance to define a lacquer. Up to within the past few years a lacquer in the public

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mind was associated with the coating on various objects of art originating in eastern countries such as Japan and China. The coating or finishing of these products, lacquering as it was called, had been developed to a fine art, and its beginnings are far back in history. The lacquer of the Japanese or Chinese is based on the juice of a native tree known as the "tsi ziu" of China or "Urushi no ki" of Japan, a species of poison sumach called "rhus verniciferus," Japanese varnish tree, and is in no sense the product of the industrial chemist. On the other hand, the present-day lacquer of the modern industrial age is distinctly the product of the research laboratory and of modern chemistry, and is an excellent example of the industrial results obtained through use of such tools.

Definition of Lacquer—Relation to Cotton

A lacquer, in the present-day sense, is a liquid material which when applied to a surface will deposit in a relatively short space of time a continuous film, through evaporation of its liquid portion. Generally, the liquid portion is an organic material and the film-forming constituent is colloidally dispersed in it. Under this definition any organic solid which will disperse in a liquid medium and deposit a film could be the basis for a lacquer, but in actual practice a modern lacquer is based on the use of cellulose nitrate for this purpose. It is through this association that cotton has become an important raw material for the manufacture of lacquers. In discussing the relation of cotton to lacquers, therefore, it is logical that the discussion should center around cellulose nitrate and its manufacture.

Cellulose Nitrate

Properties for Lacquer Use.—The historical development of cellulose nitrate since its first reported discovery in 1846 (*6*) has been covered in great detail in the chemical literature (*8*). There are, however, a number of generalized observations drawn from the empirical experience of the workers in the lacquer field that should be emphasized in this discussion. They can be summarized as follows:

1. Cellulose nitrate commonly used for lacquers is not a simple chemical compound with a definite number of nitrate groups attached to the cellulose radical. It consists of a mixture of nitrates, and its properties are a resultant of the properties of the constituent nitrates. The lacquer chemist has found by experience that the solubility characteristics of the nitrate will vary with the percentage of average nitrogen present in the product, and that for lacquer work an average nitrogen content between the limits of 11.4% N to 12.4% N gives solubilities in organic solvents best adapted to his needs.

2. Cellulose nitrate used for lacquer must be chemically stable, that is, not decompose under conditions of use over a long period of time. This

was also of utmost importance in connection with explosives, the field in which cellulose nitrate found its earliest use, and the knowledge gained in obtaining a properly stabilized product has proved invaluable in later application to lacquer work.

3. Cellulose nitrate within the nitrogen limits mentioned and dissolved or dispersed in organic solvents will deposit a clear transparent continuous film of high-tensile strength, quite flexible, and very resistant to the action of moisture and ordinary variations in temperature. The physical constants of this film, particularly permanent retention of flexibility as measured by a bend test, should be of highest value and are related to the durability of lacquers. The thickness of the film is dependent on the cellulose nitrate content of the depositing solution, which in turn is related to the viscosity characteristic of the cellulose nitrate in organic solvents.

4. The viscosity or consistency of dispersions of cellulose nitrate in organic liquids bears no relation to the chemical constants of the molecule; nitrates of the same percentage nitrogen content varying in viscosity of solution from that of water to that of heavy tar. This viscosity characteristic is apparently a property of the cellulose portion of the molecule, and at the present writing explanation of the differences lies in the field of speculative chemistry, awaiting the necessary experimental work.

Relation to Modern Lacquers.—Making use of the four generalizations given, the lacquer technologist has been able to draw up certain specifications to guide the cellulose nitrate manufacturer in the type of product which should be used; and through these, to some extent, in the selection of the type of cotton for manufacture of the nitrate. It is interesting to note that although fairly exact information on the relation between the percentage nitrogen content and solubility in organic solvents, as well as sufficient knowledge of proper means of producing stable cellulose nitrate, has been available for many years, it is only within comparatively recent years, since 1919 (*1*), that a sufficient amount of knowledge on viscosity characteristics has been obtained to permit the manufacture of cellulose nitrate below a limiting viscosity. This important discovery marked the beginning of the modern lacquer industry, since it was possible to formulate lacquers, sufficiently high in cellulose nitrate content, to be applicable in industries such as the automobile industry under practical economic conditions. The growth of the use of lacquers since that date has made the industry of some importance as a consumer of cotton.

Cotton for Lacquer Cellulose Nitrate

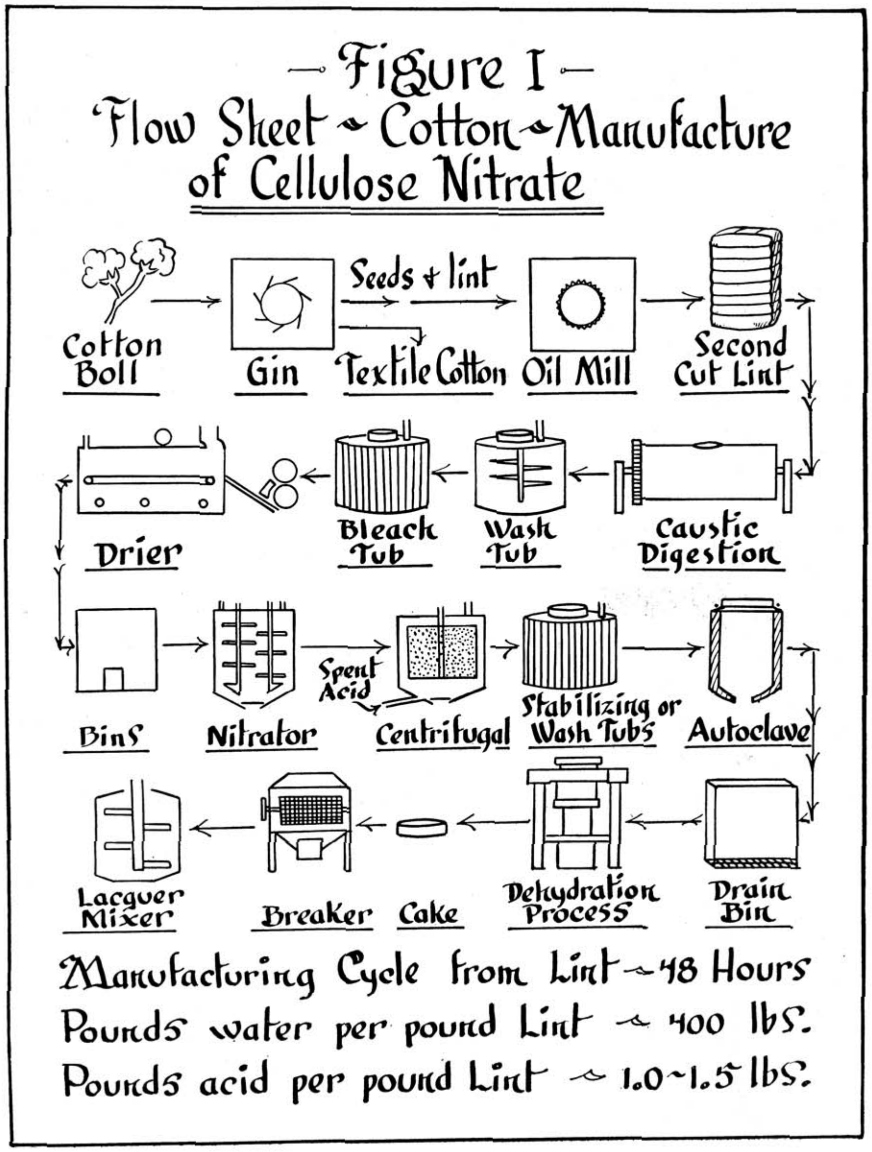
The actual selection of cotton as a source of cellulose for the nitrate of the lacquer industry bears little relation to lacquer. It is an outgrowth of the earlier uses of cellulose nitrate in the celluloid and smokeless powder industries. In the early days of the industry the manufacturer of cellulose nitrate turned to the most readily available source of cellulose of highest purity. This was dictated largely by the factor of proper stabilization of the nitrate, which was a problem of considerable difficulty, and in the case of explosives an all-important factor in proper manufacture. Cotton proved to be ideally suited as a raw material for the purpose. Its cellulose content was high, it was low in cost, uniform in composition, and unlimited in supply, three of the most important factors in the choice of any raw material for a chemical industry.

The industry, therefore, grew up around the use of cotton. In the early days cotton rovings or slivers were used, later mill-run linters, which were in use up to the time of the World War. During that period scarcity of cotton, combined with enormously increased demand, forced the industry to the use of second-cut linters, and in the later stages of the war, hull fibers. At the present time second-cut linters are in general use for the manufacture of cellulose nitrate for lacquers.

Second-cut linters have proved excellently adapted to the industry. The process of manufacture of cellulose nitrate requires as a starting point for the cellulose a raw material of certain definite staple length. This will be better understood if a brief review of the method of manufacture of cellulose nitrate from cotton is given. Figure 1 is a flow sheet showing the various steps in the handling of cotton from the raw state to the finished cellulose nitrate. It will be noted that a large number of handling operations are necessary. This mechanical handling requires a starting product capable of withstanding mechanical degradation sufficiently to retain the fibrous structure on which the handling operations are based. Not only that, but nitration is usually effected at an elevated temperature which serves further to attack the fibrous structure. The consequence is that the manufacturer of cellulose nitrate is by the nature of his process forced to select as a starting point for his cellulose, a product capable of passing through the different operations with the minimum production of fines which result in losses. It can be easily seen, therefore, that second-cut linters which are a by-product of the cotton industry as a whole are excellently adapted to the needs of the manufacture of cellulose nitrate. At the present time, even though numerous new uses have developed causing an increase in price, they still remain the primary source of cellulose used in the lacquer industry.

Composition and Treatment of Linters

Second-cut linters used in the cellulose nitrate industry come to the manufacturer in bales just as taken from the cutters in the oil mills. The lint is purchased through brokers and while no attempt is made to



— Figure I —
Flow Sheet – Cotton – Manufacture of Cellulose Nitrate
Seeds + lint
Cotton Boll
Gin
Textile Cotton
Oil Mill
Second Cut Lint
Drier
Bleach Tub
Wash Tub
Caustic Digestion
Spent Acid
Bins
Nitrator
Centrifugal
Stabilizing or Wash Tubs
Autoclave
Lacquer Mixer
Breaker
Cake
Dehydration Process
Drain Bin
Manufacturing Cycle from Lint – 48 Hours
Pounds water per pound Lint – 400 lbs.
Pounds acid per pound Lint – 1.0–1.5 lbs.

purchase on specification, advantage has been taken in recent years of the grading work of the Bureau of Agriculture in an attempt to obtain lint of definite standard for a certain price. The nitrate manufacturer is interested in the available cellulose content, and that the product will contain a minimum of dirt and trash. There has been some discussion in the lacquer industry of the advisability of selection of linters from a specified locality, but there does not seem to be any logical reason for this. Table I gives a comparison of the chemical constants of a series of samples of second-cut linters taken from various sections in the southern states. When these samples were purified and nitrated, cellulose nitrate of practically identical quality was obtained from each sample.

TABLE I

Analysis Linter Samples

Source	*Moisture**	*Ash*	*Ether extract*	*Approximate cellulose*
Chickasha, Okla.	9.07%	1.603%	0.714%	90.97%
Friars Point, Miss.	4.68	1.036	0.584	93.14
Greenwood, Miss.	8.06	1.668	1.860	90.07
Childress, Tex.	5.16	1.707	1.505	88.52
Plainview, Tex.	5.60	2.158	0.784	86.54
Dallas, Tex.	5.21	1.440	0.810	90.34
Macon, Ga.	4.92	1.318	0.950	91.12
Montgomery, Ala.	5.09	1.700	0.770	90.93
Raleigh, N. C.	6.09	1.23	0.710	90.99
Hull Fibers	7–9	2.20	2.54	77.56

* Moisture shown on air-dry basis. Others shown on bone-dry basis.

The purification process used in preparing linters for nitration consists of a mild caustic treatment in the absence of air and at elevated temperature, followed by necessary washing and bleaching treatments. In general, it follows the process commonly used to obtain a purified cellulose from any fibrous material, namely caustic treatment to remove waxy impurities followed by washing, with a final bleach treatment to obtain an absence of color. Table II gives an analysis of a typical purified cellulose obtained from cotton linters through the use of this process. For purposes of comparison an analysis of very high alpha cellulose obtained from wood

TABLE II

Analysis—Available Celluloses for Nitration

Material	*Alpha cell*	*Beta cell*	*Gamma cell*	*H_2SO_4 insol.*	*Ash*	*Ether extract*
Purified Linters	94.5%	5.0%	...%	0.25%	0.25%	0.3%
High Alpha Wood Pulp	94.0	1.5	4.5		0.10	0.15
Wood Pulp, Ordinary Grade	84.8	3.19	10.31	0.92	0.14	0.64
Wood Pulp, Special	87.5	3.5	8.5	..	0.15	..
Vegetable Fiber	95.3	3.4	0.56	0.33	0.19	0.23

pulp as well as an analysis of an ordinary type of wood pulp cellulose used in the paper trade are also given. It will be noted that a cellulose of very high purity is used in the lacquer industry.

Properties of Cotton in Relation to Cellulose Nitrate for Lacquers

Mention has previously been made that the lacquer technologist was interested in several properties of cellulose nitrate which experience had shown could be evaluated by certain empirical standards or constants, such as the percentage nitrogen content, chemical stability as measured by the resistance to decomposition at high temperatures, solubility in certain organic esters, viscosity of the solution so obtained, and finally in the physical characteristics of the film obtained from the solution. It may be of interest to touch briefly on the methods used in exercising control over these factors, and the relation of cotton in its chemical and physical characteristics to these methods.

Control of the percentage nitrogen content is not a function of the cotton cellulose. The process of nitration consists of merely allowing cotton to remain in contact with mixed sulfuric and nitric acid for a definite period of time and temperature, removing the excess acid by a centrifugal, and stopping any further reaction by immersion in an excess of water. The nitrated cellulose is then heated with water several hours to remove the water-soluble or easily decomposable esters. The ratio of nitric and sulfuric acids and water in the mixed nitrating acid, in conjunction with the temperature, determine the nitrogen content of the final product. The cotton is apparently unchanged by this treatment, fibrous character and strength of the fiber being retained. As stated by Dr. Heuser (*3*), "nitration affects cellulose, so to speak, only externally; and the molecule itself, the true framework, is not degraded. In other words the polyose character of cellulose is retained in the nitrates."

The stability of the finished nitrate is not in a strictly chemical sense directly related to the cotton used. As described above, the finished cellulose nitrate is heated with water to remove soluble or easily hydrolyzable products, until it shows no signs of decomposition at high temperatures (135°C. for thirty minutes). Provided a cellulose of high purity such as is shown in Table II is used as a starting point in the reaction, very small amounts of by-products which affect stability relations are produced. It is of course true that the nitration of a cellulose, high in oxy or hydrocelluloses may result in the formation of nitrates difficult to stabilize; but cellulose nitrate used in the lacquer industry to date has been based on high alpha cellulose, such as is so readily obtained from cotton.

Solubility of cellulose nitrate in organic esters is largely a function of the percentage nitrogen present, and this in turn as has been pointed out is controlled by nitrating acid composition and temperature. However, the viscosity of the solutions obtained, and to a marked extent the physical characteristics of the film obtained from these solutions are apparently very closely related to the molecular or polymeric structure of the cellulose used for nitration. It is in these two fields that the cotton appears to exercise a definite and marked effect on the results obtained. Unfortunately, a clear and definite picture of the relationship between chemical and physical (in the colloid sense) structure of cotton cellulose, and the properties of viscosity characteristic and film character, is not available at the present time. It is a field of research that invites the investigator, and one that should be productive not only of valuable scientific contributions but of results of practical importance in the lacquer industry as a whole.

Importance of Viscosity Characteristics

It can be stated that the modern lacquer industry owes its present growth to the discovery of commercial methods of controlling the viscosity characteristics of cellulose nitrate. Up to 1919 all lacquer products were based on cellulose nitrate which in solution gave a relatively high viscosity. For this reason a single application of solution resulted in the deposition of very thin films. In order to obtain finishes of proper service characteristics it was necessary to apply an excessive number of coatings. As soon as methods of reducing the viscosity of cellulose nitrate, while still retaining film strength and durability, were discovered and applied in the manufacture of lacquers, the use of lacquers as a finishing medium became commercially economical, and wide adoption in many fields of industry followed. The importance of this can be shown by reference to Figure 2. This curve is based on statistics published by the Bureau of Commerce. The very rapid increase in production over the years immediately following 1923, which marked the introduction of the low-viscosity type of cellulose nitrate into the commercial lacquer field, is a measure of the importance of this discovery.

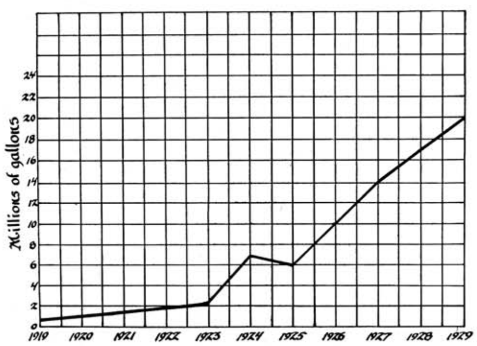


FIGURE 2.—PRODUCTION OF CELLULOSE NITRATE LACQUERS IN UNITED STATES 1919–29

Methods of reducing the viscosity of cellulose nitrate have been discussed in the technical literature (*7*) and a considerable number of patents (*1*) issued covering different processes. In general, they all require the treatment of finished cellulose nitrate, and fall into several classes comprising action of heat alone, heat in the presence of reagents of controlled alkalinity, or the action of ultra-violet light. In the modern lacquer industry the first two methods only have found commercial application.

Cellulose Viscosity and Influence on Nitrate Viscosity

Considering this reaction, which is of such practical importance from the viewpoint of the chemist, there are a number of pieces of evidence which point strongly to the influence of the cellulose molecule or complex on the result. Gibson (*2*) has shown that the viscosity of esters prepared from cellulose is governed by that of the original cellulose as measured by the viscosity of cupra ammonium solutions. The viscosity of cellulose itself can be reduced in a number of ways (*4*) (*5*), some of them paralleling the processes of reduction of the nitrate. High temperature in the presence of inert gases is satisfactory; steeping in dilute acids can be used; oxidation in the presence of water will produce low viscosity. Nitration of the finished reduced-viscosity cellulose results in the production of low-viscosity cellulose nitrate. Further striking evidence of this is the fact that regenerated cellulose produced from viscose solutions of the rayon industry when nitrated will produce cellulose nitrate of the viscosity most commonly used in the lacquer industry. The evidence is very strong, therefore, that the viscosity characteristic of cellulose nitrate of the lacquer industry is very largely a function of the cellulose complex.

This naturally raises the question as to why the present industrial methods of obtaining low-viscosity cellulose nitrate are confined to treatment of the nitrate itself. This is due to the fact that methods of treating cellulose, prior to nitration, which will produce a product of sufficiently low viscosity to be of practical commercial application, cause serious degradation of the fiber with consequent low yields and high costs.

Viscosity Characteristics and Film Character

The close connection between the viscosity of cellulose and the viscosity of the resultant nitrate may have bearing on the character of the films produced from the different types. Table III gives generalized data obtained from measurements of the physical constants of a film produced from a number of cellulose nitrates of different viscosities. These nitrates were all produced from linters of the type shown in Table II. The reduced-viscosity nitrates were obtained by heat treatment of the nitrated product. It will be noted that no pronounced tendency in differences in tensile strength have been found, but a gradual decrease in flexibility occurs as the viscosity of the nitrate is reduced. This data is offered with no attempt at explanation of the results. An interesting problem probably tied up with the factors of solvent retention and size of molecular complexes awaits solution here.

TABLE III

Relation of Physical Constants—Viscosity of Cellulose Nitrate

Viscosity	*Per cent N*	*Tensile strength*	*Flexibility*
$^1/_4$ sec.	12.00	6605	3.3
$^1/_2$	12.10	8636	9.5
$^3/_4$	11.70	9746	10.8
7	11.90	6960	23.2
10	12.40	9905	31.9
600	12.40	8912	57.0

Viscosity measured in solution of composition.

N/C	12.2%
Ethyl Alcohol	22.0
Ethyl Acetate	17.5
Benzol	48.3
	100.0%

Flexibility measured as number of bends in flexing devise to cracking.
Tensile strength—pounds per sq. inch. Film 0.003″ thick × $^1/_2$″ wide.

Commercial Aspects of Use of Cotton in Lacquers

Compared to the production of cotton as a whole, the lacquer industry is not a very large consumer of cotton. The average lacquer will contain about one pound of cellulose nitrate to the gallon. To produce this nitrate requires about one pound of linters. Based on this assumption the average consumption of cotton in the lacquer industry during the years 1926–29 is shown in Table IV. Actually the consumption is somewhat less than shown due to the fact that the industry used considerable quantities of cellulose nitrate recovered from scrap film and smokeless cannon powder. This usage is actually less than one per cent of the total available cotton produced in the United States. On the other hand, it is approximately seven per cent of the second-cut linters produced and is fifteen per cent of the total linter consumption by the chemical industry as a whole.

TABLE IV

Consumption Cotton Linters in Lacquer Industry

Year	*Gallons lacquer*	*Bales linters*	*Total production bales—U. S.*
1926	16,000,000	28,100	....
1927	17,000,000	29,800	13,000,000
1928	17,500,000	30,700	14,523,000
1929	20,500,000	35,950	14,800,000

Average bale weight—570 lb.

Future Possibilities of Use of Cotton in Lacquer

No discussion of the relation of cotton to lacquers would be complete without some attempt to forecast the future trend. At present the use of cotton linters in the cellulose nitrate industry seems firmly established. This is largely due, as has been pointed out, to the unique physical character of linters, which makes them especially adapted to the nitration process. From the chemical angle the use of other sources of cellulose is probably practicable. Table V gives physical data obtained on films produced by nitration of cellulose from wood pulp and other vegetable fiber, in comparison with films from nitrated cotton.

TABLE V

Comparison Physical Constants—Cellulose Nitrate Prepared from Cotton, Wood Pulp, and Vegetable Fiber

Source cellulose	*Viscosity*	*Per cent N*	*Tensile strength*	*Flexibility*
High Alpha Wood Pulp	20″	12.00	10,300	10.5
Cotton	20″	12.00	7,215	10.0
Regenerated Cellulose	$^3/_4$″	12.00	6,900	10.8
Cotton	$^3/_4$″	11.70	9,746	10.2
Vegetable Fiber	$^1/_2$″	12.00	7,976	10.8
Cotton	$^1/_2$″	12.10	8,636	9.5

It will be noted that film characteristics show no striking differences. The stability and service characteristics of such films are apparently satisfactory. Cellulose from these sources, however, does not lend itself to the nitration process except in the form of paper. In this form it is not as economical to use as are purified cotton linters. Until such time as the economic difference can be overcome, linters will continue to be used.

The question of the increase of use of cotton in lacquers is largely tied up with the expanding use of lacquers in industry. As shown by the curve in Figure 2 the curve of production has shown no tendency to flatten out. However, no large market hitherto untouched is in sight, and it is reasonable to assume that a slower rate of growth is in prospect. Modern industry has been quick to take advantage of the possibilities offered by lacquer, particularly in the field of mass production methods, and it can be safely stated that its adoption has occurred wherever economically feasible. It is unlikely then that any further marked increase in use will occur in the next few years. A steady growth, however, will probably continue.

Mention might be made of the possible elimination of cellulose nitrate in the lacquer industry and the subsequent effect on use of cotton. There is nothing in sight at the present time with a reasonable chance of supplanting cellulose nitrate in this field within the next few years. Certain cellulose derivatives such as the ethyl and benzyl ethers, and cellulose acetate are being examined and considered, but no loss to the cotton industry would result through their adoption or use. It is more likely that in the case of cellulose acetate, particularly, added use will be found. Synthetic resins have so far failed to find use except in conjunction with cellulose nitrate. It can probably be safely stated that continued use for cotton in the lacquer industry seems assured for some time to come.

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