Protective and Decorative Coatings

PAINTS, VARNISHES, LACQUERS, AND INKS

Prepared by a Staff of Specialists
under the Editorship of

JOSEPH J. MATTIELLO, Ph.D.
Technical Director, Hilo Varnish Corporation

VOLUME I
RAW MATERIALS FOR VARNISHES AND VEHICLES

NEW YORK: JOHN WILEY & SONS, INC.
LONDON: CHAPMAN & HALL, LIMITED
1941

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CHAPTER 20

SYNTHETIC HYDROCARBON RESINS PETROPOLS AND CHLORINATED DIPHENYLS

MARTIN BURTON CHITTICK and ARNOLD KIRKPATRICK

The term, synthetic hydrocarbon resins, can be taken to include a large number of products of widely varying composition. In this chapter we consider only two types which have attained commercial importance, one aliphatic and the other aromatic in character. Because of their dissimilarity in all but basic origin, they will be discussed separately.

PETROPOLS

Origin

The trend in the petroleum industry during the past few years has been in the direction of the chemical utilization of the hydrocarbons. This chemical phase of the industry has included the isolation of pure hydrocarbons and the synthesis of new compounds from natural gas and petroleum. Among these new compounds is a series of synthetic hydrocarbon resins which have found wide application in various industries, particularly in the paint and varnish industry.

Economic requirements in the petroleum industry made it necessary to increase the amount of motor fuel produced to a barrel of crude oil. This was accomplished by "cracking," or thermal decomposition of high-boiling hydrocarbons, usually at high pressures. Still later, with improvement in internal-combustion engines, came the necessity for fuel with higher anti-knock value. This was obtained by increasing "cracking" temperatures and pressures. As these temperatures and pressures are increased, the amount of by-product gas is increased, and the percentage of the unsaturated compounds in both the cracked distillate and the gas is increased.

In the cracked distillate, some of these unsaturated compounds are in the form of low-boiling olefines and diolefines which must be removed in order to stabilize the fuel. This is usually accomplished by polymerization resulting in a heavy viscous by-product, which upon further refinement results in the above-mentioned hydrocarbon resins.

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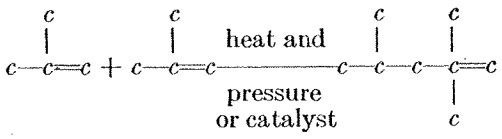
General Properties

The physical and chemical natures of these resins are so involved and complex that a theoretical consideration of them leaves much to be desired. The basic polymerization reaction entering into their production is best indicated by the following primary reaction:



Both the crude polymers and the completely refined resins consist of a large number of chemical constituents and have a wide boiling range. Vacuum distillations give a series of products ranging from

TABLE I

PHYSICAL PROPERTIES OF SOME COMMERCIAL PETROPOLS

Specific gravity $\frac{60° \text{ F.}}{60° \text{ F.}}$	0.9497	0.9923	1.025
Gravity, ° A.P.I.	17.6	11.14	10.0
Flash, C.O.C. (1)*	175° F.	230° F.	
Fire, C.O.C. (1)*	215° F.	280° F.	
Viscosity, Saybolt Univ. (2)*			
At 100° F.	200–225		
At 210° F		225–300	
Iodine number (3)*	195 min.	200 min.	200 min.
Melting point			170–190°F.
Pour point (4)*	0° F.	+ 45° F.	
Per cent solids (5)*	60–65	90–92	100
Saponification number	Trace	Trace	Trace
Unsaturates, %	99+	99+	99+
Asphaltic compounds %	0.11	0.16	0.2
Paraffin	None	Trace	Trace
Molecular weight (6)*	300	425	700
% Ash	0.005	0.012	0.02
Soluble in—			
Mineral spirits			
Benzene			
Toluene			
Xylene			
Ethyl alcohol			

* These are references listed at the end of the chapter.

a light-colored, highly volatile polymer to a dark, viscous pitch that cannot be distilled at the lowest pressures.

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The resins, as commercially marketed, vary only in their body, as measured by the Saybolt Universal Viscosimeter, and their non-volatile, or solid, content. Typical physical and chemical specifications of three grades are indicated in Table I.

Data obtained in the determination of the unsaturate of these resins by sulfuric acid absorption suggest that they are essentially non-conjugated diolefins. The relation of the specific gravity to the molecular weight indicates that these diolefins are of a cyclic rather than a non-cyclic type.

These products are thermoplastic in nature.

The volatile portion of the resins is of the same chemical nature, but of lower molecular weight.

Practical Uses

The hydrocarbon resins have found a wide application in industry, replacing drying oils as well as some of the more expensive synthetic resins.

Their drying, or curing, when used in thin films, as in protective and decorative coatings, is primarily an oxidation reaction, and comparable to drying oils. They are unique, however, in that in certain applications, particularly when baked without oxygen present, they are cured by further polymerization. Both the polymerization and oxidation are accelerated by the metal soap driers, the results being comparable to those secured with drying oils.

These resins, being hydrocarbons, are acid-, alkali-, and water-resistant and tend to impart these properties to formulations in which they are used.

They are compatible with all drying oils and with practically all other synthetics.

They have proved of special interest in aluminum vehicles, where advantage is taken of their superior leafing qualities, at the same time giving a vehicle of relatively low viscosity but of high solid content. Superior metallic luster results, and generally coverage can be secured with a smaller amount of bronze than is indicated with the conventional long-oil type vehicle.

Use is being made of the hydrocarbon resins as anti-skinning agents. In the case of those synthetics causing skinning, 15-20 per cent may be replaced with the hydrocarbon resins to eliminate the skinning and at the same time secure a better flowing product and higher luster.

The hydrocarbon resins are proving advantageous in high-

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temperature resisting coatings owing to their tendency to polymerize under heat to larger molecules and consequently better adhesion. By the same token they are useful adjuncts in baking finishes.

Most of the hydrocarbon resins form brittle films and consequently, where flexibility is required, it is necessary to use some plasticizer. Bodied fish oils or vegetable oils and the plasticizers, such as tricresyl phosphate or dibutyl phthalate, may be used successfully.

CHLORINATED DIPHENYLS

History

Diphenyl (1) and some of its chlorinated derivatives (8) were known almost three quarters of a century ago. Commercial importance, based upon practical methods of manufacture, has been attained, however, only within the past ten years.

In America the development was pioneered by the Federal Phosphorus Company, which became the Swann Chemical Company, a part of the Swann Corporation, which, in turn, was acquired by the Monsanto Chemical Company. Their chlorinated diphenyl compounds are known by the trade name, Aroclors.

A roughly parallel development took place in Germany, where I. G. Farbenindustrie A.-G. produces chlorinated diphenyls under the trade name, Clophens. Little information is available regarding the chemical composition of the various Clophens.

Method of Manufacture

Diphenyl is produced by passing benzene vapors, preheated to about 1202° F. (650° C.), over a catalyst at about 1472° F. (800° C.). The diphenyl is purified by a distillation process which provides a separation from the diphenylbenzenes of higher molecular weight formed concomitantly with the diphenyl.

Technical diphenyl ($C_6H_5 \cdot C_6H_5$) is a light-yellow crystalline solid with a freezing point of 155.3-156° F. (68.5-68.9° C.) and boiling at 491° F. (255° C.). It has a flash point of 244.4-246.2° F. (118-119° C.), (Cleveland Open Cup), and a flame point of about 284° F. (140° C.).

The diphenylbenzenes boil mostly above 680° F. (360° C.).

Chlorination is accomplished by passing chlorine into molten diphenyl, diphenylbenzene, or some mixture of the two in the presence of a catalyst. Hydrogen atoms are replaced by chlorine, and hydrochloric acid is a by-product.

$$C_6H_5 \cdot C_6H_5 + Cl_2 = C_6H_5 \cdot C_6H_4Cl + HCl$$

$$C_6H_5 \cdot C_6H_5 + 10\,Cl_2 = C_6Cl_5 \cdot C_6Cl_5 + 10\,HCl$$

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The physical properties of the final product depend upon the degree of chlorination which may be as shown in the two equations above or any intermediate point.

Various catalysts have been suggested, antimony chloride (8), iodine (9), and iron (4) being especially effective. Iron is said to have special advantage from the point of view of control during the chlorination process.

In commercial practice, diphenyl is chlorinated to give products of specific physical constants, and separation of the pure isomers is not attempted. A technical chlorinated diphenyl of 59 per cent chlorine content would not be entirely hexachlorodiphenyl but would be a mixture of penta-, hexa-, hepta-, and perhaps others. In addition to the number of chlorine atoms introduced into the molecule, the positions at which substitutions occur affect the character of the product. In manufacturing, therefore, emphasis is placed upon control of the physical properties of the batch rather than upon preparation of a particular chemical compound.

General Properties

The effect of increasing chlorine content of chlorinated diphenyls is shown by the following table. The stated chlorine contents are those of the pure compounds.

TABLE II

CHLORINE CONTENT AND PHYSICAL CHARACTER OF PURE CHLORINATED DIPHENYLS

	% Chlorine	Physical Character
Monochlorodiphenyl	18.8	Mobile liquid
Dichlorodiphenyl	36.8	" "
Trichlorodiphenyl	41.4	" "
Tetrachlorodiphenyl	48.6	Viscous liquid
Pentachlorodiphenyl	54.4	Very viscous liquid
Hexachlorodiphenyl	59.0	Soft resin
Heptachlorodiphenyl	62.8	" "
Octachlorodiphenyl	65.9	Waxy semi-crystalline solid
Nonachlorodiphenyl	68.8	Crystalline
Decachlorodiphenyl	71.1	"

The chlorinated diphenyls are chemically very inert. They do not oxidize or enter into reaction with the other resins or oils used for coatings. They are unaffected by boiling caustic soda solutions, resist the action of dilute acids, and are stable to heat for long periods up

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to 600° F. (315.6° C.) and for short periods at much higher temperatures. Below the decomposition temperature, they have little or no corrosive action on metals.

Solubility in organic solvents decreases with increased chlorine content or with increased proportions of chlorinated diphenylbenzenes.

TABLE III

COMPARATIVE PHYSICAL PROPERTIES OF COMMERCIAL CHLORINATED DIPHENYLS AND DIPHENYLBENZENES

	Chlorinated Diphenyl		Chlorinated Diphenylbenzene	
Chlorine content (Approx.)	42	60	42	60
Appearance	Thin oil	Sticky resin	Sticky resin	Brittle resin
Pour point (A. S. T. M.)	−17.7 to −20.7 C.	26 to 34° C.	.....	.....
Softening point	.....	.....	48.5° C.	100 to 105.5°C.
Distillation range (cor.)	322 to 365 C.	385° to 420° C.	Too high for A. S. T. M. Requires vacuum.	Too high for A. S. T. M. Requires vacuum.
Flash point (C.O.C.)	176 to 180° C.	Above boiling point	247° C.	None
Specific gravity	1.338 to 1.348 at 65°/15.5° C.	1.550–1.560 at 90°/15.5° C.	1.455 at 25°/25° C.	1.740 to 1.745 at 25°/25° C.
Viscosity (Saybolt seconds)	50 to 53 at 130° F.	69 to 74 at 210° F.	313.5 at 210° F.	

With the exception of the highly chlorinated crystalline products, the solubility of commercial materials is satisfactory in all the common solvents except water, glycerol, and the glycols and in the alcohols of lower molecular weight in which the chlorinated diphenylbenzenes are completely insoluble.

Volatility is extremely low and decreases with increased chlorine content. The chlorinated diphenylbenzenes are less volatile than the

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chlorinated diphenyl of equal chlorine content, as well as having higher viscosities and higher softening and melting points.

The effect of chlorine content upon both the diphenyl and diphenylbenzene compounds is shown in Table III. The data are from analyses of commercial products and not pure compounds.

The electrical properties of chlorinated diphenyl are said to be unusually good; that is, they have high dielectric constants, resistivity and dielectric strength, and low power factors. This would seem to be contingent upon complete removal of catalyst, metal chlorides, or other contaminants.

Practical Uses

Paint and Varnish. Chlorinated diphenyls are soluble in drying oils but do not themselves oxidize or polymerize. This has suggested their use in quick-drying varnishes, where the rate of hardening of the film may be regulated by the volatility of the thinner (2). Faster-drying and harder surfaces will be produced by the use of a substantial proportion of a chlorinated diphenylbenzene (5). The degree of hardness or flexibility will depend upon the hardness of the chlorinated compounds used.

Very flexible varnishes will result when a chlorinated diphenyl of about 60 per cent chlorine content is used in short-oil varnish formulations. For example, a varnish containing equal parts by weight of linseed oil, phenolic resin, and chlorinated diphenyl (60 per cent chlorine) will stand 100 per cent kauri reduction (3). In such formulas the chlorinated diphenyl is considered to act both as an oil and as a resin. The phenolic resin in the above formula may be replaced by ester gum, limed rosin, alkyd resin, or a natural resin, or the chlorinated diphenyl may be the sole resin employed. If another resin is not used, then a chlorinated diphenylbenzene of 40-60 per cent chlorine content or some mixture of one of these with a chlorinated diphenyl is to be preferred. Jenkins (5) suggests for a spar varnish 200 pounds of tung oil, 40 pounds of linseed oil, 100 pounds of chlorinated diphenylbenzene, 25 pounds of cobalt (6 per cent) linoleate drier and 400 pounds of mineral spirits.

Quick-drying house paints, made by melting chlorinated diphenyl of 54 to 65 per cent chlorine content into linseed or tung oil, adding driers, thinners, and zinc oxide, white lead, or titanium pigments, are said to have excellent durability and gloss retention. Fire-resistant paints are produced if the proportion of chlorinated diphenyl is increased to about two times the oil weight.

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The relatively high cost of chlorinated diphenyl, coupled with a high weight per gallon (12-15 pounds) would seem to restrict its use in varnishes largely to specialty items.

Although the chlorinated diphenyls are unaffected by water or alkali, they do not materially improve the resistance of the cheap resins, such as rosin and ester gum. On the other hand, when used with the more resistant resins, such as the phenolics and alkyds, they do enhance the value of these.

Plasticizers

The chlorinated diphenyls are non-solvents for nitrocellulose, but have a fair degree of compatibility and, when incorporated in lacquers, produce the effects of both resins and plasticizers. The compatibility of a commercial chlorinated diphenyl of about 42 per cent chlorine content is around 100 parts for each 100 parts by weight of nitrocelluiose. An increase of the chlorine content to 62 per cent reduces the compatibility to around 50 parts (7). The addition of ester-type plasticizers increases the compatibility. The inclusion of other resins usually decreases the amount of chlorinated diphenyl that can be added without causing blushing, tackiness, or sweating.

A principal advantage of chlorinated diphenyls lies in their excellent electrical properties coupled with gasproofness. This is made use of in preparing high-tension cable lacquers where breakdown due to the corona effect must be overcome. A suggested formula for a very flexible lacquer of this type is:

Nitrocellulose (15–20 sec.)	8.0%
Tricresyl phosphate	10.0%
Chlorinated diphenyl (42% chlorine)	7.0%
Ethyl alcohol	4.8%
Ethyl acetate	4.8%
Butyl alcohol	4.8%
Butyl acetate	23.1%
Toluene	37.5%

The chlorinated diphenyls are highly compatible with chlorinated rubber, giving increased flexibility and toughness. Their chemical resistance is similar to that of the chlorinated rubber, and the two make excellent combinations for alkali-resistant finishes. Products of 54-62 per cent chlorine content are usually recommended, although others may be used to give greater or less hardness as desired.

With ethylcellulose, a wide range of properties can be imparted by employing diphenyl or diphenylbenzenes of varying chlorine con-

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tent. The liquids or semi-liquids act as plasticizers and impart flexibility, and the more resinous products give hard compositions of good gloss and weathering resistance. The liquids cannot be used in amounts greater than 70 parts per 100 of ethylcellulose by weight without producing tackiness. For very hard weather-resistant coatings it is suggested that equal weights of ethylcellulose and a chlorinated diphenylbenzene of about 60 per cent chlorine content be used.

The chlorinated diphenyls have been added to polystyrene and other polyvinyl resins to improve fire resistance, flexibility, or hardness. Such compositions usually contain about 40 per cent of the chlorinated diphenyl and are mainly used for coatings. Molded articles, such as phonograph records, have been made from polyvinyl chloride—chlorinated diphenyl mixtures.

Moistureproofing

When small amounts (3-10 per cent) of waxes, such as paraffin, carnauba, ceresin, beeswax, montan wax, or japan wax are added to chlorinated diphenyls, the mixtures show great efficiency as moistureproofers (6). Because of a slight toxicity attributed to chlorinated diphenyls, such compositions are not recommended for moistureproofing food wrappers but are restricted mainly to the electrical field where the good electrical properties of the chlorinated diphenyls, as well as their fire-resisting qualities, are important (10). These moistureproofing compounds may be applied in a molten condition or as a solution in a volatile solvent.

The chlorinated diphenyls are insoluble in and unaffected by water, but the addition of waxes appears necessary to attain the proper physical condition for providing the highest degree of moisture resistance.

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CHAPTER 21

ARYL SULFONAMIDE-FORMALDEHYDE RESINS

ARNOLD KIRKPATRICK

HISTORY

The sulfonamide-aldehyde type of resins was first developed in Germany as a result of attempts to utilize by-products from the manufacture of saccharin (8). Although the condensation products first described were from aryl sulfonamides and formaldehyde, the reaction soon was found to be characteristic of sulfonamides and aldehydes in general.

Practical development of these products has taken place mainly in the United States, where the toluene sulfonamide-formaldehyde products have attained considerable use. Numerous patents have been issued dealing with the use of these resins in specific formulations for coatings, filaments, laminations, et cetera. Complex resins have been proposed making use of combinations of these with other types of resins. Bender (1) mixed sulfonamides with phenol and then condensed these with formaldehyde to obtain a thermosetting resin. Lauber (7) produced thermosetting resins by condensing mixtures of sulfonamides and urea with formaldehyde. Gardner and Kirkpatrick (5) developed sulfonamide-formaldehyde-alkyd resins of the thermoplastic type.

THEORY

The physical characteristics of the condensation products depend not only upon the particular sulfonamide and aldehyde used, but also upon the conditions under which the reaction proceeds. The most useful products are semi-solid or hard brittle resins, entirely noncrystalline in character. The use of acid condensing agents tends toward the formation of crystalline compounds (9). These are much less soluble and have lower compatibility with other plastic materials than do the resinous condensation products.

The exact chemical structure of the resins and the mechanism of the reactions have not been definitely established. It seems prob-

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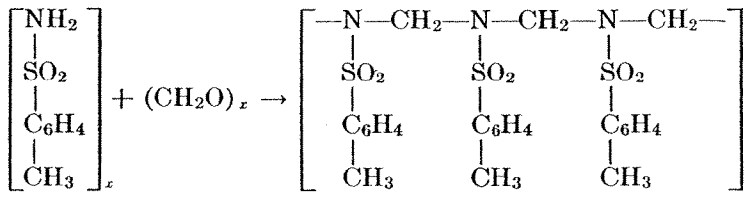
able that at least one of the reactions involves a condensation that may be represented by the equation (6):



Crystalline compounds that were separated from solutions of apparently resinous condensation products have been found to have a molecular weight of approximately 350 and seem to be composed of two toluene sulfonamide molecules attached through the nitrogen atoms by means of a methylene group. Three isomeric compounds of this structure are possible, i.e., the di-*ortho*-, di-*para*-, and *ortho-para* toluene compounds. These represent the smallest units obtainable through condensation and are probably formed by a splitting of larger, more loosely combined aggregates. Commercial resins are probably rather complex mixtures of several condensation products formed concomitantly during the manufacturing processes.

PRACTICAL USES

Varnish

Although the sulfonamide-formaldehyde resins are very soluble in most organic solvents, they are not sufficiently compatible with drying oils to make them of use as varnish materials. They have been suggested for use in what might be called spirit varnishes, to which the additions of small amounts of natural resins and oils are said to be beneficial (3). They are compatible with most other resins, and it is likely that in this case the natural resins act as mutual solvents and promote retention of the drying oil.

Lacquers

With nitrocellulose the sulfonamide resins produce lacquers of excellent depth, gloss, flow, adhesion, and fair water resistance. Solutions of the resins alone have low viscosities, and relatively large amounts may be added to nitrocellulose solutions without materially affecting the workability of the lacquer, or the hardness or flexibility of the coating.

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In general, the effect on hardness might be stated as follows:

> On the basis of 100 parts by weight of nitrocotton, the addition of resin will produce increased hardness until about 70 parts of resin are present. Then the hardness decreases slowly until 100 parts of resin are present, when the hardness will about equal that of a nitrocellulose film alone. In amounts above 100 parts of resin the hardness is reduced, reaching a minimum at about 150 parts, after which it remains fairly constant with increasing amounts.

The presence of solvent plasticizers, such as dibutyl phthalate or tricresyl phosphate in amounts below 50 per cent of the nitrocellulose weight does not change these hardness characteristics unless the amount of resin is greater than the amount of nitrocellulose. Above the one to one ratio for resin and nitrocellulose, the resin increases the flexibility imparted by a solvent plasticizer.

The sulfonamide resins are adaptable to a wide range of lacquer formulation. They blend well with almost all types of other resins, both synthetic and natural, and also with all plasticizers. Petroleum hydrocarbons do not alone dissolve them but these may be used in appreciable quantities as diluents. Alcohols are good solvents, but these appear in some cases to form loose combinations with some of the sulfonamide resins and do not dry completely. In the amounts normally used in lacquers, alcohols of lower molecular weight can be used safely in any formula where esters and ketones form the principal solvents. The resins minimize blushing characteristics and permit the use of very volatile solvent combinations.

In heat-sealing lacquers such as are used on various wrapping foils or papers, the sealing temperature can be regulated by varying the relative proportions of sulfonamide resin, plasticizer, and nitrocellulose. For a lacquer to be used at around 221° F. (105° C.) at least 75 parts of a hard sulfonamide resin and 50 parts of a liquid solvent plasticizer, such as dibutyl phthalate, are required for each 100 parts by weight of nitrocellulose. An increase in the amount of resin will lower the temperature at which sealing can be accomplished. The use of solid plasticizers gives harder lacquers that require higher sealing temperature.

Other Coating Uses

The solubility and compatibility characteristics of the sulfonamide resins have been used to increase these properties in other resins. Combinations with natural resins, alkyds, phenolics, chlorinated diphenyls, and urea resins have been suggested for use with cellulosic

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aterials and oils. The effect on the compatibility of alkyd resins eems to be especially pronounced.

Unlike most resins, the sulfonamide resins are very compatible ith cellulose acetate, giving products of great clarity, gloss, improved moisture resistance, and improved workability. Plasticizers ust be added to such compositions to give satisfactory flexibility. lthough, as with other plastics, the resins do improve the adhesive roperties of cellulose acetate, the effect is not great enough to make he acetate entirely satisfactory for general lacquer purposes.

In cellulose acetate molding compositions the sulfonamide resins re added not only to improve the appearance and working properties ut also to increase the compatibility of plasticizers (10). Such compositions are said to be improved by the addition of urea, thiourea, or uanidine (2).

The sulfonamide resins are compatible with vinyl resins. In eneral, they lower the softening temperature, improve flow, increase he effect of plasticizers, and improve adhesion.

With ethylcellulose the sulfonamide resins have a plasticizing effect ndependent of other plasticizers that may be added. Even the hardst resins add to the flexibility and toughness of ethylcellulose films.

Th crystalline sulfonamide-formaldehyde condensation products r h less soluble and compatible than the resinous products. When incorporated in nitrocellulose lacquers, these products will rystallize as the film dries, producing beautiful crystal patterns. 'or such a lacquer it has been suggested that 64 parts of resin to 100 arts by weight of nitrocellulose be used (4).

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