Compatibility of Resins with Nitrocellulose Solutions[1]

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Resins and solvents are divided into two groups, the alcohol-soluble type and the hydrocarbon-soluble type. The alcohol-type resins are most readily soluble in the alcohol-type solvents, and the hydrocarbon-type resins in the hydrocarbon-type solvents.

A few resins appear to be solvents for nitrocellulose, but most ordinary resins are not miscible with nitrocellulose under all conditions and in all solvents. This immiscibility is known as incompatibility, or "gum blush."

Compatibility is most readily obtained by the use of a resin and a solvent belonging to the same class. Incompatibility can often be relieved by the addition of a solvent complementary to that originally present in the lacquer, and in some cases by the addition of a resin complementary to that already used.

Plasticizers, which may be considered as solvents, affect compatibility in different degrees. Changing the solvent composition during the drying of the film may cause incompatibility to develop.

It was perhaps fortunate for the lacquer technologist that, when the industry commenced its present period of rapid growth a few years ago, butyl and amyl acetates were the principal nitrocellulose solvents and rosin ester was the most popular resin. These will mix with nitrocellulose in any proportions and give clear films, free from the white or turbid appearance often obtained with other resins and other solvents and commonly called a "gum blush."

When experimenters in the laboratories of the lacquer manufacturers began to try other resins than ester gum, or products closely related thereto, they experienced difficulties, as they also did when they substituted certain newly developed synthetic solvents for the butyl acetate in their usual formulas. It would be found, for example, that a certain resin gave a satisfactory solution in a given solvent, as did nitrocellulose, but that when these two solutions were mixed a cloudy lacquer was obtained, which was entirely unsatisfactory. Then it was found that the addition of certain liquids, themselves non-solvents of nitrocellulose, caused this cloudy solution to become clear, and in a number of instances the dried film deposited from the solution was clear also; but in some cases it was not. Butyl and amyl alcohols and toluene, as well as some other compounds, were heartily recommended by their makers for the elimination of this troublesome "gum blush," which was said to result from the precipitation of the resin, or gum; hence the name. However, most of the information obtained with regard to the use of certain resins, and certain solvents, in nitrocellulose lacquers has been largely empirical in nature, and is applied to new products only with difficulty, and rarely with success.

In this paper the author calls attention to the possibility of arriving at definite rules for handling solvents, resins, etc., by means of a systematic study of their properties, and presents some experimental data in support of this contention. The ideal will probably never be realized, since there are so many variables to consider, but if only a few general laws may be established, it will greatly lessen the uncertainty of lacquer formulation.

The usual dictionary definition of the word "compatibility" is "the ability to exist together in harmony or agreement" etc., and in its ordinary usage generally refers to the coexistence in harmony or agreement of two entities. But in view of the nature of the phenomenon under examination here—namely, the behavior of nitrocellulose and a resin in a solvent—it is necessary to think of this word as referring to the state of affairs existing in a system of three components. Thus, we will speak of the compatibility of ester gum with nitrocellulose in the presence of amyl acetate, and not simply of the compatibility of ester gum with nitrocellulose.

Experimental Procedure

Two parts by weight of dried 1/2-second R. S. nitrocellulose and 2 parts of resin were placed together in a glass tube with 15 parts of the solvent being examined. The tubes were corked and fastened on a slowly rotating wheel until both nitrocellulose and resin had dissolved. The solutions were then examined visually. Those exhibiting a cloudy solution were marked "X." Those which were clear were tested by flowing a small portion on a glass plate and allowing to dry, then those clear solutions which gave clear films were marked "OK" and those which dried to dull or cloudy films were marked "F."

After these preliminary tests the cloudy solutions, which were in the majority, were examined further to ascertain what type of substance improves the compatibility to the greatest extent. Since a plasticizer is almost always used in lacquers, dibutyl phthalate, chosen as representative of this class of substances, was added in the ratio of 50 per cent of the nitrocellulose present. In the cases of kauri, manila, shellac, and pontianac, tricresyl phosphate was used, as it is a better solvent for these resins than dibutyl phthalate. This caused some of the clear solutions which formerly produced cloudy films to produce clear films, but did not clear up any of the cloudy solutions.

The solutions, now containing 2 parts nitrocellulose, 2 parts resin, and 1 part plasticizer, were then divided into four portions and to each portion was added an equal volume of diluent, as follows: 95 per cent denatured ethyl alcohol, toluene, 50 per cent denatured alcohol and 50 per cent toluene, and 20 per cent butyl alcohol and 80 per cent toluene.

In one or more of these instances a clear solution was obtained for practically all resins and all solvents, but all of these clear solutions did not produce clear films. The behavior with the mixture of toluene and butyl alcohol was the same in nearly all cases as with the ethyl alcohol–toluene mixture, so the former is taken as being more nearly representative of the diluents used in actual manufacture.

Those mixtures which originally gave cloudy solutions, but which were clear and gave clear films with the addition of an equal volume of alcohol, are marked "A." Those marked "H" gave similar results when diluted with an equal volume of toluene, and those marked "M" when diluted with a mixture of 80 per cent toluene and 20 per

[1] Received November 5, 1930. Presented before the Division of Paint and Varnish Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

cent butyl alcohol (by weight). In no case did a solution fall both into the "A" group and the "H" group, but a few in the "M" group also fell into either the "A" or the "H" group.

Results

Table I shows the behavior of each of the common resins with nitrocellulose in each of the ordinary nitrocellulose solvents. These solvents are also solvents for the resins, except in a few cases, where the incompatibility is caused chiefly by the insolubility or partial solubility of the resin.

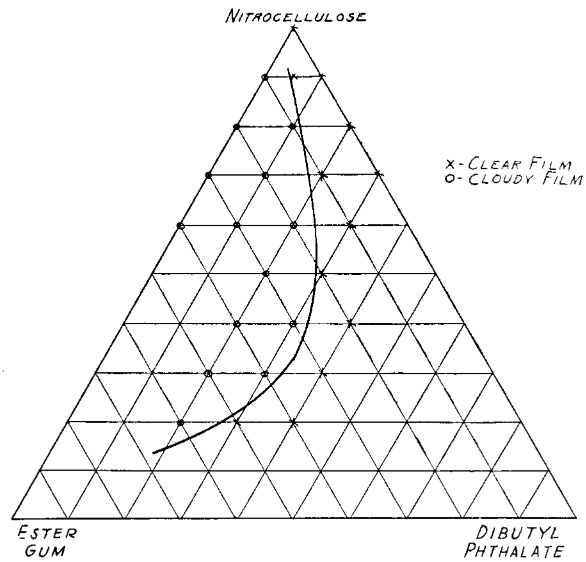

Figure 1—System Nitrocellulose–Ester Gum–Dibutyl Phthalate in the Single Solvent Cellosolve

A study of the results of these tests brings out at least two interesting points: (1) Some resins are compatible with nitrocellulose in any solvent, but the majority behave differently in different solvents; and (2) certain resins are compatible with nitrocellulose in certain solvents only when another particular solvent is present.

The resins in the first class may be disposed of briefly with the simple and logical statement that they themselves are solvents of nitrocellulose. No limited miscibility is shown, because all the components are mutually miscible in all proportions. With resins that are not actually solvents of nitrocellulose, immiscibility is experienced in the presence of certain unfavorable solvents or solvent mixtures. It is this second type of phenomenon that will be discussed in the present paper.

Mechanism of Gum Blushing

Brown and Crawford (*1*) say that "as a general rule it may be said that nitrocellulose solvents are not good gum solvents, and vice versa. Gum solvents (diluents) sometimes precipitate nitrocellulose from solution when too much of the former is added in compounding a lacquer, and a precipitation of gum occasionally occurs when an excess of nitrocellulose solvent is added to a gum solution." They also state that "many liquids which dissolve nitrocellulose are also solvents for gums and resins—but few of these liquids will hold both materials in the same mixture." Finally, they say (*2*) that gum blush "is caused by an excess of gum non-solvents (usually nitrocellulose solvents) over gum solvents in the drying film." Other writers explain the phenomenon in different ways, but the consensus of opinion seems to be that some of the resin or nitrocellulose, or both, is precipitated during the drying of the lacquer film.

These explanations are, however, not satisfactory. It is incorrect to say that the addition of a nitrocellulose solvent to a resin[2] solution will precipitate part or all of the resin. This will take place only if the added material is a non-solvent for the resin that is in solution. Whether or not this added liquid is a solvent for nitrocellulose is coincidental. As mentioned above, nearly all of the nitrocellulose solvents in common use are solvents for the resins ordinarily used in connection with them. The trouble is that the nitrocellulose and resin are not always miscible in the presence of such a solvent.

From several careful experiments and numerous observations of the phenomenon of incompatibility, the author has concluded that the troublesome phenomenon is merely a manifestation of immiscibility in a polynary system (ternary in the simplest cases) in which all of the components are not miscible with each other in all proportions. Consider the system water–ethyl ether–ethyl alcohol. Water is miscible in all proportions with ethyl alcohol; so also is ethyl ether. But water and ether exhibit only a limited miscibility. If we start with a mixture of water and ether and add ethyl alcohol, two separate phases will continue to exist until considerable alcohol has been added. However, when sufficient alcohol has been added to the mixture, a homogeneous system of three components is obtained. Even after attaining this state, two phases may again be obtained by changing the temperature of the mixture. The same effect may be obtained by adding more water or more ether. At the time two phases separate from the previously homogeneous system, each phase contains each of the three components but in different proportions. The phases usually differ in density and refractive index; hence the mixture appears turbid at first, when globules of one phase are dispersed in the other phase. When the difference in the densities of the phases and their fluidities permit, a complete separation into two clear layers takes place, each of them homogeneous, and of a definite composition depending upon conditions of temperature and relative solubilities or miscibilities.

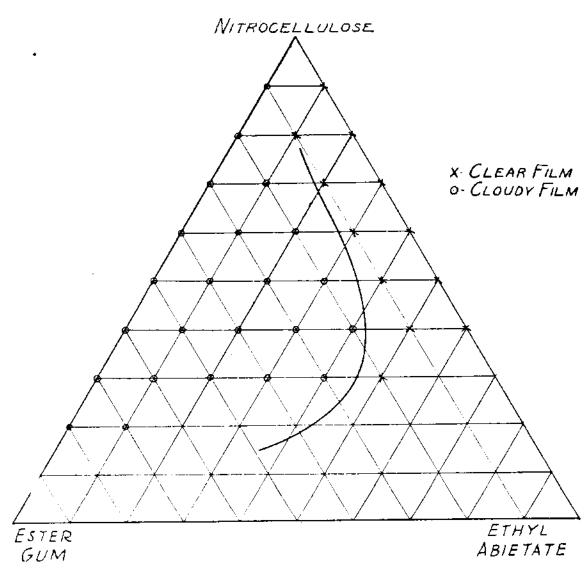

Figure 2—System Nitrocellulose–Ester Gum–Ethyl Abietate in the Single Solvent Cellosolve

The production of a turbid solution when nitrocellulose and a resin are placed in the same solvent, which may be a good solvent for each of them separately, is due to the fact

[2] The author prefers "resin" to the chemically incorrect term "gum." A gum is usually a water-soluble carbohydrate.

Table I—Behavior of Resins with Nitrocellulose in Nitrocellulose Solvents

OK—Clear solution and film.
F—Clear solution but cloudy film.
P—Clear solution and film with addition of 1 part plasticizer.
A—Clear solution and film when diluted with equal volume of alcohol.
H—Clear solution and film when diluted with equal volume of toluene.
M—Clear solution and film when diluted with 80 toluene, 20 butyl alcohol.
G—Clear solution and film with M and ester gum added.
X—Cloudy film, all tests.

Resin	Hydrocarbon Solvents					Alcohol Solvents						
	Ethyl acetate	*sec*-Butyl acetate	Butyl acetate	Amyl acetate	Butyl propionate	Acetone	Mesityl oxide	Diacetone alcohol	Ethyl lactate	Cellosolve	Cellosolve acetate	Butyl Cellosolve
Vinyl acetate	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
Rosin[a]	FP	FP	FP	FP	FP	FP	FP	OK	FP	OK	FP	OK
Ester gum	FP	OK	OK	OK	OK	M	OK	X	X	X	X	OK
Dammar[b]	OK	OK	OK	OK	OK	FP	OK	X	X	HM	HM	OK
Cumar	X	X	X	X	X	X	X	X	X	X	X	X
Amberol H-9	M	FP	FP	OK	OK	M	F	X	X	X	X	OK
Rezyl 12	OK	AM	AM	AM	AM	FP	OK	OK	OK	OK	OK	OK
Kauri	M	X	X	X	X	X	X	X	X	HM	X	OK
Pontianac	A	X	X	X	X	X	X	X	X	G	X	G
Manila	X	X	X	X	X	X	X	X	X	X	X	G
Shellac[c]	X	X	X	X	X	X	X	OK	OK	OK	X	OK

[a] Evidently contains small amount of rosin oil (hydrocarbons).
[b] Almost completely dewaxed.
[c] Bleached, waxfree.

that the nitrocellulose and resin are not miscible in all proportions. Neither is precipitated. If this were true the precipitated materials would settle, but no sediment is found. The lacquer, if such it may be called, separates into two phases, one containing most of the nitrocellulose, the other containing most of the resin. The lacquer appears milky at first, but if allowed to stand will separate into two perfectly transparent layers.

Consider as analogous to the ether–alcohol–water system described above, the system nitrocellulose–ester gum–Cellosolve (monoethyl ether of ethylene glycol). The Cellosolve is a solvent for both the ester gum and the nitrocellulose, taken separately. When the two solutions are mixed, a separation into two phases takes place, producing turbidity, or incompatibility, but if allowed to stand for some time the mixture exhibits two clear transparent layers.

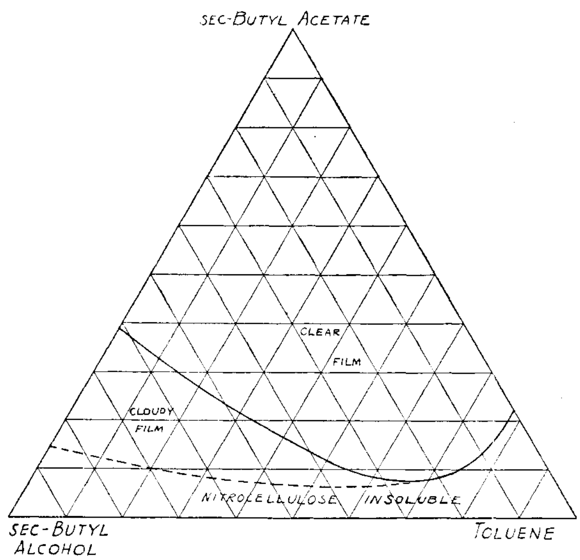

Figure 3—4 Nitrocellulose, 1 Dewaxed Dammar, 2 Plasticizer, in the System *sec*-Butyl Acetate-*sec*-Butyl Alcohol-Toluene

That the state of affairs existing in this mixture is similar to that in immiscible ternary systems of ordinary organic compounds is further demonstrated by the fact that when some of this turbid mixture is warmed to about 50° C. it becomes clear and homogeneous. It can also be cleared up by the addition of another suitable compound. It is well known that even small amounts of a fourth component materially displace the equilibrium of ternary systems. The fourth component may be another resin, but is usually another solvent, or a plasticizer, which may be considered a non-volatile solvent.

Effect of Nature of Resin and Solvent

In order to study the combinations of solvent and resin which produce clear films in the presence of nitrocellulose, the various resins and solvents have been divided into two groups—alcohol-type and hydrocarbon-type. The usual aliphatic esters are classed under the hydrocarbon-type, because they behave more like hydrocarbons than alcohols. The compounds containing a hydroxyl group are naturally classed as alcohol-type, as are the ketone solvents. Resins are classed according to their solubility in hydrocarbons or alcohols (*3*). Some resins are soluble in both hydrocarbons and alcohols, and in such cases the classification is made according to chemical structure or composition (*4*). In general, a solvent belongs to the alcohol class if it will dissolve refined shellac, and to the hydrocarbon class if it will dissolve cumar (coumarone) resin. A resin is in the alcohol-soluble class when it is almost completely soluble in 95 per cent ethyl alcohol and in the hydrocarbon-soluble class when it is almost completely soluble in toluene.

The more important solvents and resins are classified as follows:

Alcohol-Type	Hydrocarbon-Type
Solvents	
Ethyl alcohol	Toluene
Butyl alcohol	Xylene
Amyl alcohols	Petroleum naphtha
Acetone	Ethyl acetate
Mesityl oxide	Butyl acetates
Diacetone alcohol	Amyl acetates
Cellosolve	Butyl propionate
Cellosolve acetate	*sec*-Hexyl acetate
Butyl Cellosolve	
Ethyl lactate	
Resins	
Shellac	Cumar
Kauri	Ester gum (rosin ester)
Pontianac	Dammar
Sandarac	Amberol resins (phenol-formaldehyde)
Manila	
Glyptal resins (Rezyls)	

By referring to the data of Table I it will be noted that when incompatibility exists in a mixture of nitrocellulose, resin, and solvent, the situation is often remedied by the addition of a solvent of the type opposite to that already present. For example, the cloudiness in a mixture of nitrocellulose, kauri, and Cellosolve (an alcohol-type solvent) can be cleared up completely by the addition of toluene (a hydrocarbon-type solvent). The same holds true to a lesser extent with resins. A lacquer made of nitrocellulose, pontianac, and Butyl Cellosolve gives a turbid or heterogeneous film, even when toluene, etc., are added to the solution. But the same lacquer will produce a clear film if some ester gum (a hydrocarbon-type resin) is added. The effect of alcohol-type and hydrocarbon-type ingredients appears to be complementary. This is not surprising, however, in view of the known effect of alcohol and hydrocarbon mixtures on the solubility of nitrocellulose (5).

Effect of Plasticizer

Having thus examined qualitatively the incompatibility phenomena existing in certain lacquer solutions, let us consider the effect of varying the proportions of some of the ingredients, such as might take place in the actual formulation or manufacture of a nitrocellulose lacquer.

As pointed out previously, a solution containing nitrocellulose and a resin, which produces a cloudy or heterogeneous film upon drying, may be caused by the addition of a plasticizer to produce a clear and homogeneous film. That the effect depends upon the nature of the plasticizer as well as the amount added is shown by Figures 1 and 2. These charts represent graphically the behavior of various

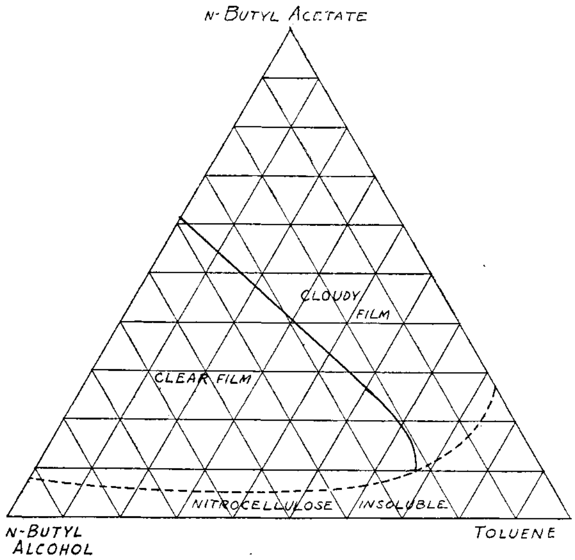

Figure 4—50 Nitrocellulose, 50 Bleached Shellac, in the System *n*-Butyl Acetate-*n*-Butyl Alcohol-Toluene

mixtures of nitrocellulose, resin, and plasticizer, all dissolved in the single solvent, Cellosolve. In both cases the resin is ester gum, and the plasticizer is dibutyl phthalate in Figure 1 and ethyl abietate in Figure 2. A test was made at each point of the chart indicated—a circle indicates that a cloudy film was produced, and a cross, a clear film. These charts show that, with this particular solvent, in order to obtain a clear film, the maximum plasticizer is required when the nitrocellulose and resin are present in approximately equal quantities, and that dibutyl phthalate is somewhat more effective than ethyl abietate in this respect.

Effect of Solvent Composition

A lacquer solution may be perfectly clear and homogeneous, but deposit a very bad cloudy film upon drying. The phenomenon familiarly called blushing is divided into three distinct kinds—the hydrocarbon blush, the moisture blush, and the gum blush. Only those vagaries of solvent composition which cause gum blush to develop in the evaporating lacquer film will be discussed here.

The development of gum blush when a clear lacquer solution evaporates is due to the widely different rates of evaporation of the solvent constituents. In the original solution the ratio of ester-alcohol-hydrocarbon (or whatever the solvents may be) is correct for obtaining compatibility between the nitrocellulose, resin, etc. But after a portion of the solvent has evaporated, it may be found that the concentration of one component, inimical to good compatibility, has greatly increased with respect to the others. Whether the component which increases in concentration—and one of them must increase except in the rare instances of constant-evaporating mixtures—is an ester, an alcohol, or a hydrocarbon depends upon the relative evaporation rates of the individuals present; and whether such an increase in the concentration of one of the solvent ingredients will cause incompatibility to develop will depend upon the nature of the resin present in the lacquer. Thus an increase in the relative concentration of alcohol as the solvent evaporates will probably cause trouble with certain hydrocarbon-type resins, and likewise an increase in the concentration of a hydrocarbon solvent will cause trouble with an alcohol-soluble resin. Examples of these two possibilities are given in Figures 3 and 4.

In Figure 3 the solid ingredients are 4 parts nitrocellulose, 1 part dewaxed dammar resin, and 2 parts plasticizer. The solvent mixtures used were composed of *sec*-butyl acetate, *sec*-butyl alcohol, and toluene, in various proportions, as represented by points on the chart. It will be seen that after the concentration of alcohol in the original solvent mixture is increased beyond certain limits, an incompatibility develops during the drying on account of the excess of alcohol, which is hostile to the compatibility of nitrocellulose with dammar (a hydrocarbon-type resin), even in the presence of considerable plasticizer. Solvent mixtures, represented by points above the dotted line, dissolve the given lacquer ingredients to a clear solution.

In Figure 4 the solid ingredients are equal parts of nitrocellulose and bleached, dewaxed shellac, and the solvents, butyl acetate, butyl alcohol, and toluene in various proportions. In this case we find that good results are obtained only when the concentration of alcohol is above a certain limit. When the concentration of butyl alcohol is less than the minimum (about 20 per cent in this example), the relative concentrations of butyl acetate and toluene, both hydrocarbon-type solvents, increase to the point where incompatibility results during the course of evaporation.

The experimental results recorded in Figures 3 and 4 confirm the previous observation that compatibility is obtained most readily by using an alcohol-type solvent with an alcohol-soluble resin, and, vice versa, a hydrocarbon-type solvent with a hydrocarbon-soluble resin.

Literature Cited

(1) Brown and Crawford, "Survey of Nitrocellulose Lacquer," p. 9 (1928).
(2) *Ibid.*, p. 19.
(3) Calvert, Ind. Eng. Chem., **21**, 213 (1929).
(4) Hofmann and Reid, *Ibid.*, **21**, 955 (1929).
(5) Hofmann and Reid, *Ibid.*, **20**, 687 (1928).

The Sugar Situation in China—The latest reports state that there are ten sugar refineries and six sugar factories in China, the great bulk of the sugar being made by small mills employing crude processes. The three qualities are green (dark brown), brown (light brown), and white. The sugar is dark brown as it comes from the brewing vats and is bleached by exposure to the sun. The green and brown varieties are only slightly bleached, and the white is subjected to an extended bleaching process. The five kinds of sugar imported into China are brown, white, refined, cube or loaf, and rock or sugar candy. The brown sugar is mixed with native sugar and also goes into cheap confectionery, to bakers, and to native doctors. The white sugar is used in the better-class households and for higher-priced candies, cakes, and pastries. Sugar candy is imported in sacks and is repacked into cartons and tins upon arrival and is in high favor as a gift.