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UNIVERSITY OF LOUISVILLE

FACTORS INVOLVED IN IMPROVING THE BLUSH RESISTANCE OF LACQUERS

A Thesis
Submitted to the Faculty
of the Graduate School
in Partial Fulfillment of the
Requirements for the Degree of
Master of Chemical Engineering

Department of Chemical Engineering

By

Franklin D. Snyder

1938

FACTORS INVOLVED IN IMPROVING

THE BLUSH RESISTANCE OF LACQUERS

Director: Dr. R. C. Ernst

Approved by Reading Committee:

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The

Author Wishes

To Acknowledge His

Appreciation

For All The Kind and Valuable Aid

Given by Dr. R. C. Ernst,

Who Directed This Research.

INTRODUCTION

It is the purpose of this thesis to study the many factors involved in improving the blush resistance of lacquers.

The property of improved blush resistance can be accomplished in many ways. Which method, or combination of methods, is employed, will depend upon the basic formulation of the particular lacquer used, and the market price of the various lacquer solvents.

By the proper application of the findings of this thesis, many lacquer thinner formulations may be materially reduced in cost, with no sacrifice in the quality of blush resistance.

All the practical findings of this work have been proved by application to, and use in, commercial lacquers.

HISTORICAL

The general impression that lacquers are comparatively new is erroneous. An examination of the literature shows that nitrocellulose was first prepared in 1833 (24). In 1855 a patent (8) was issued for the use of a solution of nitrocellulose as a coating material for fabrics, paper, and leather. The next year (1856) a patent was issued (8) for a composition of nitrocellulose, resin, castor oil, and a coloring matter. This last is essentially the composition of a modern lacquer.

Many factors retarded the growth of the lacquer industry. A few of the most important were;

(a) A scarcity and lack of suitable solvents for nitrocellulose.

(b) Small quantities of nitrocellulose produced very viscous solutions, and consequently the lacquers solid content was very low.

(c) Lacquers were rapid drying, so that their application was solved satisfactorily only upon invention of the spray gun.

(d) A general lack of suitable equipment for the manufacture of lacquers.

(e) A lack of education of the general public to the advantages of lacquers.

(f) The cost of lacquers was relatively high compared to other coatings.

Only after a method was found to materially reduce the viscosity of nitrocellulose (14), enabling a relatively high solid content to be obtained, did lacquers become popular.

As a result of scientific investigation, these retarding factors have been over come; and today lacquers have an undisputed place in the field of protective coverings.

THEORY

There are three distinct types of blush that can be distinguished from one another only by examination under the proper conditions. They are:

(a) Cotton Blush

This results when the solvents in a lacquer are not properly balanced, and an excess of the nonsolvent is built up in the drying film. This type of blush can be easity remedied by adding a small quantity of a slowly evaporating, active solvent.

(b) Gum Blush

This may be caused by the imcompatibility of the resin with nitrocellulose, or precipitation of the resin in the drying film, because of the improper solvent balance or selection. This is one of the most difficult types of blush to remedy.

(c) Water Blush

This is caused by the absopption heat by the vaporizing liquids. The resultant temperature may be below the dew point of the air. In which case the precipitated moisture is emulsified in the drying lacquer film. If the film has set before the minute drops of water evaporate, the continuity of the dried film is broken and a whitening results. This blushing varies in intensity with the temperature and the humidity. That is, it is much worse on hot humid days.

Of the three types of blush mentioned, this work will be devoted solely to an investigation of water blush. A superficial examination of the problem seems to indicate the use of large quantities of slowly evaporating solvents. This is not practicable for three reasons.
They are:

(a) The drying time of the lacquer may be slowed beyond the practical point for production finishes.

(b) Slowly evaporating solvents are expensive; therefore the formulation may not be economical.

(c) A full understanding of the many

other factors involved, will help remedy the blushing of lacquers without greatly slowing the drying time or increasing the cost.

The average lacquer at spraying consistency contains 75 to 80 per cent of volatile matter which is relatively expensive. Therefore, it is easily understood why the economics of lacquer thinner formulation is such an important factor.

Much has been published concerning the solvent power and evaporation rate (1-3, 5-7, 9-13, 15-20, 22, 23) of various solvents; but virtually nothing has been published that will give the lacquer formulator a comprehensive picture of the many factors that will help improve blush resistance

METHOD OF CONDUCTING TESTS

All lacquers, except where noted, were prepared by dissolving one and one-fourth ($1\frac{1}{4}$) pounds of wet R. S. $\frac{1}{2}$ Second Nitrocellulose (70% dry nitrocellulose, 30% denatured alcohol) in one gallon of the specified lacquer thinner.

When weather conditions were favorable (hot, humid days) the lacquers were flowed simultaneously on a glass plate and observed for whitening. In all cases check runs were made.

The composition given for all lacquer thinners is in per cent by volume.

MATERIALS

All solvents, resins, and nitrocelluloses used in these tests were commercial products.

The products used and their physical constants were as follows:

SOLVENTS

Acetone

Distillation Range 56° to 57.5° C.

Specific Gravity 0.792

Amyl Acetate

Distillation Range 120° to 145° C.

Ester Content 92%

Specific Gravity 0.868

Butanol

Distillation Range 114° to 118° C.

Specific Gravity 0.811

Secondary Butanol

Distillation Range 94° to 106° C.

Specific Gravity 0.810

Butyl Acetate

Distillation Range 116° to 128° C.

Ester Content 90% to 92%

Specific Gravity 0.875

Secondary Butyl Acetate

Distillation Range 108° to 118° C.

Ester Content 85% to 88%

Specific Gravity 0.864

Cellosolve

Distillation Range 130° to 136° C.

Specific Gravity 0.930

Denatured Alcohol

Distillation Range 74° to 80° C.

Specific Gravity 0.810

Ethyl Acetate

Distillation Range 70° to 80° C.

Ester Content 85% to 88%

Specific Gravity 0.884

Ethyl Acetate

Distillation Range 75° to 80° C.

Ester Content 98%

Specific Gravity 0.900

Fusel Oil (Amyl Alcohol)

Distillation Range 110° to 135° C.

Specific Gravity 0.811

Isopropyl Acetate

Distillation Range 84° to 93° C.

Ester Content 85% to 88%

Specific Gravity 0.869

Isopropyl Alcohol

Distillation Range 78° to 85° C.

Specific Gravity 0.808

Methanol

Distillation Range 63° to 65° C.

Specific Gravity 0.797

Methyl Ethyl Ketone

Distillation Range 78° to 82° C.

Specific Gravity 0.805

Toluol

Distillation Range 109° to 111° C.

Specific Gravity 0.867

Troluoil

Distillation Range 96° to 128° C.

Specific Gravity 0.732

Xylol

Distillation Range 133° to 145° C.

Specific Gravity 0.857

RESINS

Beckacite #1114

Rosin maleic anhydride glycerol ester.

Specific Gravity 1.17

Color I-K

Melting Range 193° to 102° C.

Ester Gum

Rosin glycerol ester

Specific Gravity 1.14

Color N-WG

Melting Range 65° to 72° C.

Teglac Z-152

Rosin maleic anhydride glycerol ester.

Specific Gravity 1.14

Color N

Melting Range 140° to 150° C.

PLASTICIZERS

Bakers' No. 15 Castor Oil

Blown castor oil.

Specific Gravity 0.995

Dibutyl Phthalate

Ester Content 99% to 100%

Specific Gravity 1.050

Tricresylphosphate

Specific Gravity 1.180

Boiling Point 285° C. at 10 mm.

NITROCELLULOSE

R. S. ½ Second Nitrocellulose

Nitrogen Content 11.8% to 12.2%

Specific Gravity 1.65

RESULTS

A. Influence of Resins

For this test four lacquers were prepared, one containing no resin and three containing resin in weights equal to the dry nitrocellulose content.

The resins used were the following:

(1) Ester Gum

(2) Beckacite #1114

(3) Teglac Z-152

The solvent retention of each resin was lower in the above listed order. These three resins are representative of the average hard resin used in lacquer formulation. They were selected because of their wide commercial use and because a single solvent combination could be used for preparing the lacquers.

Volatile Composition by Volume

8% Butanol

16% Butyl Acetate

16% Ethyl Acetate

60% Toluol

This solvent line up is representative of the type generally used for the spray application of lacquers.

Blushing is increased in the following order:

(1) Ester Gum

(2) Beckacite #1114

(3) Teglac Z-152

(4) No Resin

B. Influence of Plasticizers

For this test four lacquers were prepared, one containing no plasticizer and the other three containing one-half (½) the amount of the dry nitrocellulose of the following:

(1) Dibutyl Phthalate

(2) Tricresyl Phosphate

(3) Bakers' #15 Castor Oil

No difference in the blushing of the three lacquers containing plasticizer could be detected.

All three were considerably better than the lacquer containing no plasticizer.

This is quite logical because plasticizers are non-volatile solvents for nitrocellulose.

C. Influence of Slowly Evaporating Solvents

Several of the more slowly evaporating solvents were investigated. The composition of the volatile portion of the lacquer was as follows:

8% Butanol

16% Solvent under investigation

16% Ethyl Acetate

60% Toluol

Blushing increased in the following order:

(1) Secondary Hexyl Acetate

(2) Amyl Acetate

(3) Secondary Amyl Acetate

(4) Butyl Acetate

(5) Secondary Butyl Acetate

(6) Cellosolve

These results are in very close agreement with the only other published work that could be found on this subject (21).

D. Influence of Rapidly Evaporating Solvents.

In all spraying lacquers, except in special cases, there is at least a small amount of rapidly evaporating solvent. If no rapidly evaporating solvent were used, there would be very little, if any trouble with water blush. However, from the standpoint of the economics of lacquer formulation, this is impracticable. Also because of their excellent solvent power, rapidly evaporating solvents materially reduce the viscosity of the lacquer.

At the present time, only three rapidly evaporating solvents, in the same price range, are commercially available.

Blushing increased in the following order:

(1) Isopropyl Acetate

(2) Ethyl Acetate

(3) Methyl Ethyl Ketone

E. Influence of Water Soluble Components.

There were three references (20, 21, 22) in the literature to the adverse effect of water soluble components in lacquer formulations on blush resistance.

In order to check this point, the following formulations were tested.

8% Butanol
16% Butyl Acetate
8% Ethyl Acetate
8% Component under investigation.
60% Toluol

Blushing increased in the following order:

(1) Isopropyl Alcohol
(2) Denatured Alcohol
(3) Methanol
(4) Acetone

A lacquer in which the water soluble component was replaced with Ethyl Acetate was much superior to the one containing isopropyl alcohol.

Therefore, it was decided to make a test of 85% and 98% ester ethyl acetates.

As was expected the one containing 98% ethyl acetate was superior.

These experiments show the very detrimental effect of having water soluble components in the lacquer thinner.

F. Influence of Higher Alcohols.

Lacquers were prepared with the following composition:

8% Higher Alcohol
16% Butyl Acetate
16% Ethyl Acetate
60% Toluol

Blushing increased in the following order:

(1) Fusel Oil (Amyl Alcohol)
(2) Butanol
(3) Secondary Butanol

C. Influence of Nitrocellulose Dehydrated with Butanol

Since water soluble components have an adverse effect on the blush resistance of lacquers, a test was made to emphasize the fact further.

Two lacquers were prepared with the following compositions.

LACQUER #1

125# Butanol Dehydrated Nitrocellulose
(70% dry Nitrocellulose, 30% Butanol)
8 Gal. Butanol
16 Gal. Butyl Acetate
16 Gal. Ethyl Acetate
60 Gal. Toluol

LACQUER #2

125# Nitrocellulose Dehydrated with Denatured Alchhol
(70% dry Nitrocellulose, 30% Den. Alcohol)
2½ Gal. Butanol
16 Gal. Butyl Acetate
21 Gal. Ethyl Acetate
60 Gal. Toluol

These two lacquers are of identical composition, except that in Lacquer #2 the denatured alcohol was replaced with an equal weight of ethyl acetate.

As was to be expected Lacquer #1 was far superior to Lacquer #2 in blush resistance.

H. Influence of Excess Tolerance

For this test three lacquers of the following solvent composition were prepared:

LACQUER #1

8% Butanol
16% Butyl Acetate
16% Ethyl Acetate
60% Toluol

LACQUER #2

7% Butanol
14% Butyl Acetate
14% Ethyl Acetate
65% Toluol

LACQUER #3

8% Butanol
16% Butyl Acetate
16% Ethyl Acetate
45% Toluol
15% Troluoil

In this test lacquer #1 was quite definitely superior to Lacquers #2 or #3.

This is readily understood when it is considered that the excess tolerance of Lacquer #1 is higher during the drying period. Therefore, it flows longer, giving the water more opportunity to escape and the pores to close.

Using petroleum diluents similar in evaporation rate to toluol (such as troluoil), a great improvement in blush resistance can be made, over Lacquer #1. As an example the following is given:

10% Butanol
30% Butyl Acetate
10% Ethyl Acetate
50% Troluoil

The primary reason for improved blush resistance is, that, although the initial excess tolerance was not so high as Lacquer #1; the excess tolerance during the evaporation period increased more rapidly.

I. Influence of Slowly Evaporating Diluents

In this test two lacquers of the following solvent composition were prepared:

LACQUER #1

10% Butanol
20% Butyl Acetate
10% Ethyl Acetate
60% Toluol

LACQUER #2

10% Butanol
20% Butyl Acetate
10% Ethyl Acetate
50% Toluol
10%-10° Xylol

Lacquer #2 was superior in blush resistance to Lacquer #1.

In using this method to improve blush resistance, care had to be exercised. That is more of the slowly evaporating solvent had to be used to compensate for the slower evaporation of the Xylol.

As an example, there would be a danger of cotton blush if five per cent (5%) less butyl acetate were used in Lacquer #2.

J. Influence of Replacing Butanol with Slowly Evaporating Esters.

Three lacquers of identical composition except that the butanol was replaced with slowly evaporating esters, were prepared.

They were:

LACQUER #1

8% Butanol
16% Butyl Acetate
16% Ethyl Acetate
60% Toluol

LACQUER #2

24% Butyl Acetate
16% Ethyl Acetate
60% Toluol

LACQUER #3

8% Secondary Hexyl Acetate
16% Butyl Acetate
16% Ethyl Acetate
60% Toluol

No difference in blush resistance could be detected between Lacquers #1 and #2. However, Lacquer #3 was decidedly superior to the other two.

These results were decidedly contrary to popular opinion among lacquer formulators, who have believed for years that butanol was a powerful blush inhibitor.

When these three lacquer thinners were made into complete lacquers and three coats applied to wood panels, formulas #2 and #3 did not flowout so well.

The basic lacquer formulation was:

100# R. S. ½ Second Nitrocellulose
50# #1114 Beckacite
30# Dibutyl Phthalate
100 Gal. Lacquer Thinner

The reasons why Lacquers #2 and #3 did not flow so well might be:

(1) Lowering of surface tension by butanol.

(2) Formation of constant evaporating mixture by butanol and toluol, increased the excess tolerance

as the film dries.

(3) A combination of #1 and #2 .

These findings were verified verbally by Charles Bogin of Commercial Solvents Corp., when the matter was discussed in their laboratories in Terre Haute, Indiana.

K. Spray Out Vs. Flow Out Tests.

Several commercial lacquers were sprayed and flowed on wood panels and observed for blush.

In all cases the flow out tests were much more severe than the spray tests.

This is quite logical in view of the fact that about 30% of the lacquer thinner is lost between the gun and the work(4). A substantial part of this 30% is rapid evaporating solvents.

The only exception to this rule is where ethyl cellosolve is used as the slow evaporating solvent. In this case the flow out tests were superior to the sprayed panels.

CONCLUSION

Conclusion

If the blush resistance of a lacquer is not sufficiently good, there are many ways to help improve it. Which method, or combination of methods, will be the most economical will depend upon the market price of the various solvents.

Factors that will help improve blush resistance are:

(1) Use a resin of higher solvent retention. This is not practicable because it would change the basic formulation of the lacquer.

(2) Use of beneficial plasticizers. This method is not practicable for the same reason as given above.

(3) Replacement of part or all of the fast evaporating solvent with a slower one.

(4) Replace the slowly evaporating solvent with a slower one.

(5) Replace the regular nitrocellulose with one dehydrated with butanol.

(6) Replace the water soluble components with water insoluble components. If for any reason this is not possible, use methods #3, #4, and #5.

(7) Replace Butanol with a higher molecular weight alcohol such amyl alcohol.

(8) Replace part of or all of the hydrocarbons with slower evaporating ones. When using this method, care has to be excerised to keep the thinner properly balanced by method #3 or #4, or by a combination of #3 and #4.

(9) Replace the butanol with a very slowly evaporating solvent such as amyl acetate, cellusolve acetate, as secondary hexyl acetate. This method is not practicable because poor flow results.

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