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SUBJECT: IMPROVEMENT IN SPRAYING PROPERTIES OF METALLIC "DUCO" ENAMELS

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PARLIN LABORATORY REPORT NO. 968

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INTRODUCTION

For some time means have been sought to reduce mottling in metallic "Duco". The search was recently given impetus by the growing demand for brighter, more metallic colors. These colors could be obtained by increasing the metallic flake content, but this aggravated mottling tendencies. Uniformity of color of a metallic finish has been obtained in the trade by spraying a very dry last coat; the immediate setting-up of the film reduced the motion of the metallic flake thus minimizing mottling. There are two objectional features to this practice, (1) an extra coat that adds little to the total film build is required, and (2) the poor flow of a dry coat increases the amount of buffing required.

Mottling as it develops in "Duco" may be described as the formation of light and dark areas that vary in ease of detection with the viewing angle. Mottling as used in this report covers two varieties: (1) "salt and pepper" mottling in which the light and dark areas are very small and (2) "dapple" mottling in which the contrasting areas may be an inch or more in diameter.

This report deals with the work done on the causes and the prevention of mottling. It covers the development of an effective mottling inhibitor and the evaluation of the effect that the addition of the requisite amount of the additive has on the general film properties of "Duco" metallics.

PATENT STATUS

U. S. Patent 2,467,858 assigned to General Electric Company appears to cover the use of G.E. Silicone 81069 in coating compositions to control flow and film characteristics. It is assumed that the control of mottling of metallic finishes is in that category.

Confidential Information

The metallic coating compositions involving the use of the silicone liquid for control of mottling are considered embraced by Schedule B of the C.I.L. /du Pont Agreement and, therefore, the report may be distributed accordingly.

SUMMARY AND CONCLUSIONS

Mottling is apparently caused by variations in the orientation of the aluminum flake during drying of the finish. An area in which the flake is largely perpendicular to the surface appears dark, while those areas in which the flake is largely parallel to the surface appear light. The orientation is dependent on the viscosity of the medium, rate of evaporation of the solvents, and surface tension of the medium which would affect leafing of the aluminum flake.

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The initial investigatory work was in effect an effort to control one or more of the above factors. The experiments undertaken and the results obtained are summarized below:

I. Reformulation of the thinner on a faster evaporation basis resulted in some slight improvement.

II. Removal of the organic acid (citric or malic) normally present in metallic "Duco" resulted in slight improvement but the results were inconsistent. Further work was anticipated on this phase but never carried out when the much more promising anti-mottling agent was uncovered.

III. Substitution of other aluminum flake, both of the leafing and non-leafing varieties, resulted in no improvement when substituted on a comparable tint strength basis.

IV. Addition of ethyl cellulose and dynamite nitrocellulose causes only very slight improvement.

V. Addition of "Daktose B" was fairly effective in decreasing mottling but the improvement was counterbalanced by a deleterious effect on other film properties.

VI. Addition of General Electric's Silicone 81069 to a metallic "Duco" completely halts vortex action eliminating the resulting salt and pepper mottle. A small addition, 0.02-0.05%, of G.E. 81069 (C-679 in C-158) on the final product completely stops mottling, flooding, or streaking of the aluminum when metallics are applied by dip or flow coating. While this addition does not eliminate completely the formation of contrasting light and dark areas on very wet spray application, it does considerably lessen the contrast and affords generally more uniform color conditions when variations in wetness of application develop.

VII. Exhaustive tests to evaluate the effect of the addition of silicone on other properties were made and there was no consistent evidence that any properties were adversely affected by this addition with the possible exception of "scaling" when buffed excessively.

VIII. Parlin Release Letter No. 412 was written to recommend that field tests be made on the Fisher-Chevrolet production line at Flint, Michigan. The tests were thought to adequately demonstrate the potential advantages of the anti-mottling agent. Reduction in mottling and improved flow were apparent results. Another advantage which should become more apparent with continued usage, particularly where the bodies and the sheet metal parts for automobiles are sprayed in different locations under varying conditions, is the reduction in color variations between wet and dry spray obtained by the use of the anti-mottling agent.

IX. A supplementary release is in preparation recommending use of the anti-mottling agent in the prescribed manner

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in all automotive and refinish metallics deemed objectional in mottling characteristics by the Laboratory and the Sales Department.

EXPERIMENTAL

Factors Influencing Metallic Mottling

If the drying of a metallic "Duco" film is observed under a microscope, it becomes apparent that individual aluminum flakes have no attraction for each other or for particles of pigments. The important factor in final film appearance seems to be mobility of the flake.

The movement of the flake within the film is caused by convection currents set up in the drying film by the evaporation of the solvents and by the settling of the flake. As the solvent evaporates from the drying film, the viscosity increases. The medium eventually becomes too viscous for the convection currents to move the flake and they are trapped into position. If the film is applied sufficiently wet for vortex action to fully develop, a honeycomb appearance results which is known as "salt and pepper" mottling. In vehicles of the proper viscosity characteristics and surface tension, a sufficient number of the flakes carried to the surface by convection currents are held there forming a near continuous metallic film. This is known as leafing. For the large part sprayed lacquer films are too viscous and dry too rapidly for full vortex patterns to develop or for leafing to have much effect on the appearance of the dried finish. Thus it appears that "salt and pepper" mottle or partial leafing are relatively unimportant factors, leaving the cause and cure of the dapple effect as the primary objects of this study.

When a metallic lacquer is sprayed, the aluminum flake strikes the surface in a random but uniform manner. Three forces effect the maintenance of the flake in this uniform condition: (1) the viscosity of the medium controls the mobility of the flake, (2) the force of application and gravity effects tend to drive the flake to the panel-finish interface, and (3) the convection currents tend to lift the flake to the finish-air interface. On very dry application the viscosity of the medium is such that no motion of the flake is possible and a uniform finish results. But such a procedure is not practical. As the degree of wetness of application is increased, it becomes increasingly difficult to maintain uniform application and to maintain a uniform balence of forces 1, 2 and 3 throughout the finish. Wherever this balence is upset a change in color results from the change in orientation of the aluminum flake.

The first attempts to control mottling were efforts to control the viscosity of the lacquer as it reached the surface of the panel. A standard metallic and application procedure was established and used throughout the tests reported (see Appendix I).

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I. Thinner Reformulation

Several different solvent mixtures as well as single solvents were studied as thinners. By using sufficient amounts of low boilers such as methyl acetate and toluene in certain proportions, it was possible to obtain adequate evaporation between the gun and the work to precipitate the lacquer as it reached the surface. This eliminated mottling, corroborating the theory but, of course, was not practical because of appearance of the film. No thinner combinations were formulated which offered sufficient foolproofness to overcome the non-uniformity of spray inherent in normal application. It was found possible to slightly improve uniformity of color by careful control of the solvents and diluents in the thinner which evaporate in the middle of the range for lacquer solvents. Some loss in flow characteristics generally accompanied this improvement.

II. Removal of Organic Acid

Organic acids such as citric (G-499) and malic (G-678) are added to "Duco" as a gelation inhibitor as well as for other reasons. It was hoped that the removal would cause an increase in the viscosity of the lacquer as it came in contact with the work sufficiently to halt the motion of the flake. The effectiveness of the removal was influenced by the length of the storage period prior to application; the explanation of this observation was not immediately evident. This lead was to have been followed, but was dropped with the advent of the silicone oil.

III. Use of Other Aluminum Flake

It was considered possible that other types of flake might be less influenced by the mottling forces. Several other types including the non-leafing varieties were studied. In all cases where the flake was substituted in the standard composition at an equal "metallic effect", mottling of a comparable degree was observed.

IV. Ethyl Cellulose and Dynamite Nitrocellulose as Additives

These materials were considered as additives because of their viscosity characteristics and because ethyl cellulose is known to be an anti-flocculating agent. Some improvement was realized from the addition of ethyl cellulose. However, the solubility of ethyl cellulose limited the addition to a solution at 10% solids, a factor which rather radically reduced the solids content of the metallic "Duco" when an amount sufficient to reduce mottling was used.

Spray-outs of a metallic "Duco" to which a small amount of a solution of dynamite nitrocellulose had been added were covered with small specks. These were identified as undissolved dynamite nitrocellulose.

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V. Addition of "Daktose B"

The composition, preparation, and use of this compound as an anti-mottling agent in "DULUX" metallics is covered in Philadelphia Laboratory Reports #912 and #926 prepared by L. K. Osdal and issued April 6, 1948 and June 29, 1948, respectively. Its use in "Duco" metallics resulted in some improvement in mottling. Several disadvantages developed from this add, however, and these counterbalanced the improvement. These are:

1. Development of false body followed by grit formation.
2. Flocculation of some pigments causing gloss decrease and fine grit formation.
3. Excessive embrittlement of the finish after short periods of accelerated aging.
4. Marked decrease in the viscosity of the enamel on aging resulting in a loss of anti-mottling effect.

These factors probably result from the degradation of the nitrocellulose caused by a reaction with the amino group in the "Daktose B" molecule.

VI. Addition of Silicone Oils

Silicone oils produced by General Electric Corporation and Dow Corning Corporation are sold to the Paint and Lacquer Industries as anti-flooding and flow-out agents. Addition of 0.01% of G.E. Silicone 81069 completely halts metallic flooding, vortex pattern formation and improves the flow of the metallic "Duco" if applied by dip or flow coating. Spray-outs on 4 x 12 inch panels and on 11 x 12 inch panels showed surprisingly little improvement in mottling to be gained by the addition. Further puddle pour and flow-coating studies showed that the silicone completely halted all motion of the metallic flake in the lacquer medium just as though the viscosity was suddenly increased to the gel point. In order to study more closely spray application, the test panel size was increased. Automobile doors and flat panels, 30 x 36 inches, were used as test panels, and the material was applied just as solid color "Duco". Over this larger area it is more difficult for the sprayman to maintain absolutely uniform application and mottling becomes more apparent. While the silicone addition did not eliminate mottling, it both decreased the amount of dapple development and lessened the contrast (the light areas were not as light nor the dark areas as dark) in the mottled areas. The silicone addition thus allows standard color quality at increased wetness of application. Improved flow with decreased buffing and increased film build per coat are important advantages with current metallics.

Tests were next made to determine (1) the amount of the addition for optimum improvement under carefully controlled conditions and (2) the effects on mottling of varying these conditions with the following results:

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1. A 0.05% add on basis of total lacquer was selected as the optimum addition from a four-step ladder of additions from 0.01% to 0.10%. This 0.05% addition on the metallic "Duco" is equal to the following weight parts of G.E. Silicone S1069 for each 100 weight parts of the lacquer components listed based on the standard testing metallic given in Appendix I.

   A. 20 parts of G.E. S1069 for 100 parts of aluminum flake.

   B. 1.0 part of G.E. S1069 for 100 parts of aluminum tinting enamel.

   C. 0.14 part of G.E. S1069 for 100 parts of lacquer solids.

   D. 0.05 part of G.E. S1069 for 100 parts of metallic "Duco".

2. The addition of 0.05% of silicone affords some improvement in mottling under any spray conditions except extremely dry application. The silicone-containing metallics were consistently more uniform in color than standard when applied as solid color "Duco" (conditions of medium wetness). When sprayed very wet almost to the point of sagging the standard material was less uniform but mottling in both was too bad for the finish to be acceptable.

While there is some evidence that the anti-mottling agent's effectiveness is slightly increased if added in the manufacture of the tinting enamel, this gain is not considered adequate to offset the simplification realized by the addition of the silicone solution in the manufacture of the finished product from the tinting enamels. The mixing required to blend these is considered adequate to disperse the silicone.

Representative Dow Corning silicones from the DC 200 Fluid series were chosen to cover the viscosity range available for testing against G.E. Silicone S1069. Our tests showed that smaller amounts of those DC Fluids in the 100-500 centistoke viscosity range were required to halt vortex action in metallics. This difference was not observed in decreased mottling on large sprayed areas. Since studies to determine the effect of the addition of the requisite amount of the G.E. Silicone were underway, no further testing of the DC Fluids was considered worthwhile unless some unsatisfactory qualities in the G.E. oil were encountered.

VII. Effect of Silicone on "Duco" Properties

So far as can be determined by laboratory tests, the inclusion of G.E. Silicone has no detrimental effect on the following "Duco" properties:

1. Solids/viscosity relationship.
2. Stability of wet sample.
3. Spraying characteristics other than mottling.

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4. Gloss
5. Flexibility
6. Film hardness.
7. Adhesion to substrate or intercoat adhesion.
8. Blister resistance.
9. Cold-crack resistance.
10. Outdoor durability (6 months).
11. Adhesion of refinish coat to exposed finish containing silicone.

These tests were run with varying amounts (including the 0.05%) of G.E. Silicone 81069 against undoped "Duco" according to Parlin test methods.

There are two important properties that are affected that may present problems on production line.

1. If a metallic lacquer is divided into two portions and the anti-mottling agent is added to one and if the two lacquers are sprayed wet in accordance with TM-95C, the color cards will not match. If the last coat of each is applied dry, the two cards will match but neither card sprayed as directed in TM-95C will match the dry spray-outs. The motion of the aluminum flake which is halted by the high viscosity of dry spray-outs or decreased by the presence of the silicone in wet spray-outs accounts for these color differences. By adjusting the aluminum content experimental and standard can be matched for any given degree of wetness of application. There is less change in color of the experimental with changes in application conditions. The advantage of increased color uniformity should become more apparent with continued usage, particularly where the bodies and sheet metal work are sprayed in different locations under different conditions or on patching.

2. In spite of the fact that G.E. Silicone 81069 minimizes mottling, it does not in the least reduce "sealing" (i.e., rings of contrasting color produced when the finish is buffed through from one coat to the next). There is some evidence that color contrast in sealed areas might be slightly worse in silicone-containing metallics. However, with the improved flow and build possible through application of wetter coats of uniform appearance less buffing should be required and less instances of cutting through the thicker coat experienced.

In an effort to explain the effect of the silicone, some of the more important physical properties of the doped "Duco" were compared with standard. The G.E. Silicone 81069 does not retard rate of drying as determined by the Gardner Circular Dry Time Recorder or by evaporation rate studies in accordance with Parlin test method.

On the volatile portion of the formula surface tension is lowered by 3-5% by the addition of the silicone; this is not

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considered sufficient to fully account for the improvement in flow and in mottling characteristics. Viscosity studies with the Brookfield Viscosimeter indicate that thixotropic or plastic effects are not responsible for the improvement. Viscosities of standard and experimental were comparable and normal.

VIII. Field Tests

Parlin Laboratory Release Letter No. 412 was written to recommend a production line test of the anti-mottling agent in 287-55255 Ice Green "METALLI-CHROME" on the Fisher-Chevrolet line at Flint, Michigan (see Appendix II for formulation). The initial tests were made from pressure pots and a single body including the sheet metal parts was sprayed. The Fisher Body representative instructed that this material be sprayed much wetter than usual and that it be followed up by a body sprayed with regular material in the same manner. This gave a three-way comparison of the anti-mottling material sprayed wet versus standard material sprayed both wet and dry. In this test the silicone-containing material exhibited far less mottling than did standard sprayed wet and was even superior to regular production (i.e., standard sprayed dry). Since the anti-mottling material had been sprayed wet, the film was smoother than normal production and required less buffing. G.M. spraymen and polishers commented on the improved working properties of this material.

On the basis of this test Fisher Body charged their system with the new material. Examination of approximately 50 finished bodies revealed that as a whole they represented a very marked improvement over standard in mottling characteristics.

IX. General Release

As a result of the successful field test Parlin Supplementary Release Letter No. 412-A was written to recommend use of the anti-mottling agent as prescribed in the parent release letter to cover all metallic formulations which the Laboratory and Sales Department deem inferior in mottling characteristics.

More recent tests have shown that 0.025% G.E. Silicone 81069 might be approximately as effective as the 0.05% prescribed. Later, after additional field experience is gained, this reduction in silicone content will be given consideration. This would lower the cost of the silicone addition to 1¢ a gallon and lessen the decrease in lacquer solids which accompanies the add.

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APPENDIX I

Standard Testing Metallic

246-051	45.0%
214-083	5.0
B-613	50.0
	100.0%

Test Procedure

Standard testing metallic is formulated to contain anti-mottling agent. Standard and experimental are thinned with 37608 to 22-23 seconds viscosity in a Zahn #2 cup. Automobile doors or panels (30" x 36") are prepared by coating with the standard automotive undercoats. Topcoat is applied from pressure pot using 20#/in.^{2} fluid pressure and 70#/in.^{2} air pressure. Two coats were applied at the wetness of solid color "Duco". Panels were baked 20 minutes at 185°F. then buffed. Polished panels were compared for mottling.

Following this procedure the standard testing metallic exhibits considerable dapple mottle.

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APPENDIX #2

260-55255 ICE GREEN "METALLI-CHROME" SPECIAL ANTI-MOTTLING

253-0751	25.6%
253-0484	12.5
253-0785	.8
253-0376	2.4
208-081	7.2
J-G-100-X-10241	2.4
B-614	5.0
B-613	44.1
	100.0%

Wt./gal.: 7.96 lbs. @ 25°C.

Visc.: 45-60" 15 cup @ 25°C.

Anal. Solids: 32.8%

Note: Batch must receive a minumum of 2 hours thorough mechanical agitation to insure adequate dispersion of B-614. Hand-mix batches must receive equivalent agitation.

I.C.C. Class: Liquid
Flash Point: 20-80°F.

PATENT MARKING: This material must be labeled or stenciled "U. S. Patent 2,335,760"

J-G-100-X-10241 SILICONE SOLUTION

KG-4072	2.0%
H-583	98.0
	100.0%

Wt./gal.: 7.17 lbs. @ 25°C.

Solids	
KG-4072	2.0%

For information re Parlin Laboratory Release Letter No. 412.

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