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Marshall Laboratory
December 10, 1954MEMORANDUM REPORT NO. M-746PREPARED BY C. W. Secker, H. R. HeikelUNIVERSAL TINTING BASESObjective:

To develop a line of tinting colors which will be compatible with both orthodox oil-type finishes and emulsion finishes of the O/W type.

Background:

During the development of the Custom Color System, a decision was made by Sales to include a latex emulsion to the three alkyd whites already formulated. Tinting of all whites was to be done with a single line of colorants. However, the alkyd colorants which had been formulated for the alkyd whites were not compatible with 391-012 "Flow Kote" White. It was recognized that this dual compatibility could be accomplished either one of two ways:

1. by reformulating the line of alkyd colorants, which was considered the soundest, but the most time consuming and,
2. by formulating a new type of "Flow Kote", doped with the proper ingredients to make it compatible with the existing alkyd colorants.

Because of the close time table, along with the urgent need for a latex finish to be included, the second approach was followed, and a Custom Color Flow Kote was developed which could provide 320 of the total 572 Custom Colors involved. Its initial cure, however, was inferior to 391-012 and to date all eleven batches of the deep tone Custom Color Flow Kote have fallen off for color development after from 3 to 6 months aging, possibly due to an inactivation of the surface active agents by adsorption on the pigment surfaces.

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Advantages:

By replacing the "632-Line" Custom Color Tinting Bases with the proposed Universal Tinting Bases, we will eliminate the need for the special Custom Color "Flow Kote" Whites and allow the use of a standard type of "Flow Kote", similar to 391-012 (only an adjustment in the hiding level should be necessary). In addition, we should be able to provide more of the 572 colors available. Simplification of existing tinting lines and simplification of plant tinting practices could be a long range advantage of this project.

Theory:

In developing a Universal Tinting Base, the following three components are important:

1. Vehicle
2. Pigment
3. Surface Active Agent

Vehicle: The most important requirement for a vehicle in a Universal Tinting Base is that it should be one, which itself has the characteristics of surface activity, that is, one portion of the molecule should be hydrophilic (water-loving) and the other portion hydrophobic (oil-loving). The balance of these two portions of the molecule along with the degree of its surface activity determine its usefulness. However, vehicles which do not have surface active characteristics can be used if some surface active agent is incorporated with it. Other requirements, as good grinding characteristics, proper viscosity for optimum dispersion with the paint vehicles, cure, color retention, shelf stability and effect on brushing must be considered.

Pigment: From a universal standpoint pigments fall into two distinct classes:

1. Inorganic pigments, which are hydrophilic by nature and,
2. Organic pigments, which are hydrophobic by nature.

The mechanism for tinting with each pigment type appears to be quite similar; the pigment particle is wetted with vehicle in the grinding process which forms an envelope around the surface of the particle. When this vehicle-coated particle is introduced into an emulsion, one of two things probably happens:

1. The oil on the surface of the pigment particle, for all practical purposes is emulsified, leaving the pigment particle now uncoated. If the uncoated particle is hydrophilic, as in the case of inorganic pigments, it tends to migrate to the external or water phase, where it tints. If the uncoated pigment particle is hydrophobic, as is the case with organic pigments, it tends to migrate to the internal or latex-oil phase. This causes poor color development, since the pigment must be in the external or water phase to tint. If a hydrophilic surface active agent is

present either in the white or the color base, the mechanism is probably modified, in that the uncoated pigment particle adsorbs some of this wetting agent on its surface. This action would leave the inorganic pigment more hydrophilic and the hydrophobic organic pigment now hydrophilic, depending upon the amount of surface active agent present.

2. The vehicle-coated pigment, on being introduced into the emulsion or beforehand in the grinding process, is itself coated with the proper surface active agent to make it hydrophilic. This differs from the first case, in that the vehicle is not emulsified. The particle is not uncoated but has an envelope of wetting agent around both the pigment particle and the vehicle. This wetting agent must be hydrophilic in order to carry the vehicle-coated particle into the external or water phase to tint. Therefore in this case it makes no difference whether the pigment is organic or inorganic. This second consideration appears to be possible only if there is a difference between migration into the latex phase and the added vehicle phase from the standpoint of color development.

Surface Active Agent: These are compounds in which one portion of the molecule is hydrophilic and the other portion is hydrophobic, thereby forming a bridge between oil-type materials and water-type materials. The balance of the two portions of the molecule determines its relative affinity for either hydrophilic or hydrophobic materials. Basically these compounds fall into three general classes. If the molecule tends to ionize, the surface active agent is said to be cationic or anionic. It is cationic when the oil-soluble portion of the molecule is the positive ion and anionic when the oil-soluble portion is negative. When the surface active agent does not ionize the agent is non-ionic. From our work thus far a non-ionic type of wetting agent gave the best results. Cationic and anionic surface active agents appear to be interfered with by the ions already present in the emulsions. In addition to being non-ionic, the surface active agent must be hydrophilic to carry the pigment or vehicle-coated pigment particle into the external phase.

Summary of Completed Work:

In order to be considered universal, the bases which were formulated had to be compatible in the following products:

639-776	Custom Color Gloss Deep
639-780	" " Semi-Gloss Deep
639-778	" " Flat Deep
389-007	" " "Flow Kote" Deep
391-012	"Flow Kote" White
389-001	PVA Sealer Coater
P-389-U-94425	Rhoplex Sealer Coater

These whites were tinted to the 28/1 deep tone color level and brushed out on pearl board. The brushout was subjected to a rub-up test to determine if crocking developed and a flow-out was made indicating color development in the can. In order to be considered good for

compatibility, maximum color had to develop in the can. If color development in the can was good, brushouts and rub-ups were usually good. The panels were also recoated overnight. By taking into consideration these four factors, brushout, initial and overnight, rub-up and flow-out, the overall appearance of the panels was rated as follows:

- 5 = excellent (flow-out matches brushout; no rub-up)
- 4 = good (flow-out matches brushout; only slight rub-up)
- 3 = fair (Flow-out light to brushout; also slight rub-up)
- 2 = poor (flow-out indicates incompatibility, however, brushout develops some color)
- 0 = no good (Completely incompatible).

Since the proposed universal tinting bases eventually are to be used as replacements for the present "39-Line" Custom Color Bases, it was necessary that the pigment concentrations should remain the same for corresponding bases in both lines, in order to eliminate variations in tinting strength. Following is a list of the pigments used and their corresponding concentrations:

<u>Inorganic Pigments:</u>		<u>%</u>
W-679	Chrome Yellow Lt.	74.2
W-630	Ferrite Yellow	63.7
W-622	Molybdate Orange	63.4
W-895	Red Iron Oxide	47.4
W-303	Red Iron Oxide	70.2
<u>Organic Pigments:</u>		<u>%</u>
W-527	Monastral Blue	20.1
W-300	B.O.N. Red. Dk.	30.8
W-785	Monastral Green	26.3
W-205	Lampblack	22.4

We began by grinding these pigments on formulas similar to the "39-Line" formulas, the only difference being that the RC-601, Soya P.E. resin was replaced on a weight basis with KH-5186, Kelsol (Spencer-Kellogg's Ammoniated Linseed Oil), which is both a drying and water dispersible oil.

While these bases were compatible with the alkyd and "Flow Kote" whites, they were not compatible with either the PVA or Rhoplex Sealer Coaters. For this reason we decided to incorporate some surface active agent, which when used in conjunction with Kelsol would improve compatibility in the Sealer Coater formulations. The following surface active agents were examined with this end in mind:

1. H-609, Triton X-100, an alkylated aryl polyether alcohol, which is non-ionic.
2. KH-5185, Triton 770, a sodium salt of alkylated polyether sulfonate, which is anionic.

3. DS-23858, Nacconol NRSF, alkyl aryl sulfonate, which is anionic.
4. G-414, Duponol M E., sodium lauryl sulfate, which is anionic
5. DS-26332, Ethomeen C-20, a tertiary amine having one fatty alkyl group and two polyoxyethylene groups substituted on the nitrogen. This agent is cationic
6. Ethofats - mono-fatty or resin acid esters of polyethylene glycols. These agents are non-ionic.
 - (a) D.S.-27693 Ethofat 142/60 (ethylene oxide portion equals 50 moles).
 - (b) DS-26115 Ethofat 142/15 (ethylene oxide portion equals 5 moles).
7. Tamol 731 (35% soln) - believed to be the sodium salt of dicarboxylic acid with a long alkyl chain. This agent is anionic.

These agents were incorporated into the grinds at approximately 5% by weight on the total base and of the above series H-609, Triton X-100 showed the best results, giving us compatibility in the Sealer Coater formulations to some extent. However, in order to improve the compatibility still further, we decided that an investigation of other vehicles besides Kelsol would be of value. Below is a list of other materials we looked at as possible vehicles for our Universal Tinting bases:

1. G-12 Soya Lecithin
2. H-630 Rheotol
3. KH-5187 Glyceryl Mono Riccinoleate
4. H-156 Dehydrated Castor Oil
5. H-154 and H-534 Oleic Acid and Triethanolamine
6. H-22 Castor Oil
7. H-481 Tween 81
8. DS-27716 Non-Break Safflower Oil
9. H-253 Raw Linseed Oil
10. H-59 Soya Varnish Oil
11. A.D.M.'s U.T. Oil #4

Grinds in these vehicles were spot-checked in our tinting whites for compatibility both with and without the use of Triton X-100 and of the above list we selected the following materials as showing the most promise as a universal vehicle:

1. KH-5186, Kelsol (Spencer Kellogg's Ammoniated Linseed Oil, a water-soluble drying oil.
2. KH-5187, Glyceryl Mono Riccinoleate, a non-drying, non-ionic, hydrophobic wetting agent.

3. H-156, Dehydrated Castor Oil, a semi-drying oil, having some surface active characteristics.

4. H-481, Tween 81, Atlas' Polyoxyethylene Sorbitan Mono Oleate, a non-drying, non-ionic, hydrophilic wetting agent.

In order to evaluate these four materials more properly, a complete series of grinds was prepared, in which all the pigments of interest to us were dispersed in each of the four vehicles on formulas similar to the present "39-Line" bases. In addition, another series of grinds was prepared using these vehicles, however in this case, an arbitrarily set amount of 5% Triton X-100 was added. Inorganic pigmented bases were given 2 passes on a 5 roll mill with organic pigmented bases being ground 24 hours conventional S.U.W. at a 40/80 ratio. Fineness of grind of these bases was approximately 1.0 mils.

All white bases were tinted with these series of color bases to the 28/1 fl. oz. level, checked for compatibility and overall appearance and given a numerical rating. A summary of the results obtained for each vehicle and vehicle/wetting agent combination for both the inorganic and organic grinds is shown in the following tables:

TABLE I. INORGANIC PIGMENTED BASES: (W-679, W-630, W-622, W-895, W-303)

<u>Vehicle</u>	<u>639-776</u>	<u>639-778</u>	<u>389-007</u>	<u>391-012</u>	<u>389-001</u>	<u>P-389-U-94425</u>	<u>Total</u>	<u>Aver.⁽⁴⁾</u>	<u>Rated⁽⁵⁾</u>
	<u>22⁽¹⁾</u>	<u>19</u>	<u>20</u>	<u>23</u>	<u>0</u>	<u>13</u>	<u>97⁽³⁾</u>	<u>3.23</u>	<u>F</u>
Kelsol	22	23	25	23	12	22	127	4.23	G
Kelsol & Triton	23	22	22	25	5	21	118	3.93	G
GMR	20	18	22	23	24	21	128	4.27	G
GMR & Triton	24	24	22	25	3	7	105	3.50	F
DCO	24	24	21	24	18	18	129	4.30	G
DCO & Triton	25	24	24	25	18	24	140	4.67	E
Tween	25	24	17	23	21	19	129	4.30	G
Tween & Triton	25 ⁽²⁾	25	25	25	25	25	150		

TABLE II. ORGANIC PIGMENTED BASES: (W-527, W-300, W-785)

<u>Vehicle</u>	<u>639-776</u>	<u>639-778</u>	<u>389-007</u>	<u>391-012</u>	<u>389-001</u>	<u>P-389-U-94425</u>	<u>Total</u>	<u>Aver.</u>	<u>Rated</u>
Kelsol	15	15	13	10	2	7	62	3.44	F
Kelsol & Triton	14	14	13	8	7	8	64	3.56	G
G.M.R.	0	0	5	6	0	5	16	0.89	NG
G.M.R. & Triton	0	0	5	6	2	4	17	0.94	NG
DCO	14	15	12	9	2	0	52	2.89	F
DCO & Triton	11	12	13	10	9	7	62	3.44	F
Tween	15	15	14	10	2	12	68	3.78	G
Tween & Triton	15	15	14	11	2	11	68	3.78	G
Maximum	15	15	15	15	15	15	90		

TABLE III. INORGANIC AND ORGANIC PIGMENTED BASES:

<u>Vehicle</u>	<u>639-776</u>	<u>639-778</u>	<u>389-007</u>	<u>391-012</u>	<u>389-001</u>	<u>P-389-U-94425</u>	<u>Total</u>	<u>Aver.</u>	<u>Rated</u>
Kelsol	37	34	33	33	2	20	159	3.31	F
Kelsol & Triton	36	37	38	31	19	30	191	3.98	G
GMR	23	22	27	31	5	26	134	2.79	F
GMR & Triton	20	18	27	29	24	25	145	3.02	F
DCO	38	39	34	34	5	7	157	3.27	F
DCO & Triton	35	36	34	34	27	25	191	3.98	G
Tween	40	39	38	35	20	36	208	4.33	G
Tween & Triton	40	39	31	34	23	30	197	4.10	G
Maximum	40	40	40	40	40	40	240		

Explanation of the Above Tables (See Table I.):

(1) Total of the brushout ratings in each white base for the number of pigments involved in this particular vehicle or vehicle/wetting agent combination.

(2) Maximum rating if all brushouts were rated excellent for the number of pigments involved.

(3) Total of the brushout ratings for the number of pigments involved in all 6 whites tested, for the particular vehicle or vehicle/wetting agent combination.

(4) Arrived at by dividing the total described in #3 by the number of whites times the number of pigments involved. (Ex. In Table I, the average is obtained by dividing the total by 30.)

(5) Letter ratings for the average by our rating system.

Comments on the Above Tables:

1. In all cases, compatibility in the Sealer Coater formulations was improved by the addition of Triton X-100 to the vehicle. This was especially true in the case of 389-001, PVA Sealer-Coater. The exception was Tween 81, which showed good compatibility even without the addition of Triton X-100.

2. It should be kept in mind that the Triton X-100 level used in preparing the color bases was arbitrarily set at 5% on the total base. Compatibility in some cases could be further improved by raising the Triton level above 5%. This is especially true with the (DCO & Triton) bases.

3. Although the inorganic pigmented bases with GMR and (GMR & Triton) were compatible with the alkyds, the organic pigmented bases in these vehicles were not compatible. W-300 and W-785 dispersions in these vehicles were very poor, probably due to exceeding the GMR tolerance of the alkyds.

4. 391-012 "Flow Kote" is only slightly better for compatibility over 389-007 Custom Color "Flow Kote" Deep, however, the latter contains approximately 0.4#/gal. of added wetting agent.

5. A marked improvement was noted using Rhoplex Sealer-Coater over PVA Sealer-Coater with respect to compatibility.

6. Use of straight Tween 81 as the grinding vehicle gave the best results for compatibility for both the inorganic and organic pigmented bases. Running a very close second was the combination of (Tween 81 and Triton). About equal for third and fourth was (Kelsol & Triton) and (DCO & Triton). (DCO & Triton) organic pigmented grinds appeared to be low in tinting strength in the alkyds. However, later work indicated that this tinting strength problem was due to the method of dispersion (SRL vs. SUW) rather than to the nature of the dispersing vehicle.

Scrubability and Wet Adhesion:

To check the effect on scrubability and wet adhesion of the color bases dispersed in these vehicles or vehicle/wetting agent combinations, tints were made with the W-527 pigmented bases at the 28/4 fl. oz. deep tone level in 389-007 and 391-012, (the maximum tinting level in our present Custom Color System). Brushouts were made on wallboard panels that had previously been coated with Primer Sealer and Flat Wall Paint. These panels were aged for one week and subjected to the standard Marshall Laboratory scrub test, using a 5% soln. of T.S.P.

All panels except those tinted with the (DCO & Triton) grind of W-527, showed complete failure after only 200 cycles. Those tinted with the (DCO & Triton) grind showed almost no failure after 2000 cycles, at which the testing is said to be complete. Untinted 389-007 and 391-012, used as controls, were also intact after completion of 2000 cycles. Failure, where noted, appeared to be due to lifting of the film and in some cases due to the solubilizing of the film in the T.S.P. Soln. Failure of the films which contained (DCO & Triton) appeared to be due to erosion at a point where the film was defective initially.

In addition, a series of stains, which included ink, #2 soft lead pencil, Mongol Red pencil #966, China-Marker Red 169-T, were made on the panels and cleaned with both Ivory soap and scouring powder. Most of the stains could be removed with soap, the ink and China-Marker Red stains being removed by mild rubbing with scouring powder. In most cases the film was not appreciably damaged by this action.

Drying, Sag Resistance and Gloss:

Because of the far superior results obtained with the (DCO & Triton) combination in our scrub tests and the knowledge that the compatibility of the bases dispersed in this vehicle/wetting agent combination could be improved by raising the Triton level, we decided to adopt this combination as the dispersion medium for our Universal Tinting Bases. To determine the effect on drying, sag resistance and gloss with this combination, we added to the three alkyd whites amounts of these ingredients approximately equal to what they would contain if tinted to the 28/4 fl. oz. deep tone color level. The doping was done for color bases which would possibly contain up to 15% Triton on the total base. Also included were similar dopings with RC-601, soya/P.E. alkyd resin to simulate "632-Line tintings. The untinted whites were used as controls. Results of these tests are shown in the following table:

TABLE IV

	<u>Tack Free</u>	<u>Dry Thru</u>	<u>Sag</u>	<u>60° Gloss</u>
639-776	8 hrs.	10 hrs.	18 mm	90
639-776 + RC-601	9 "	10 "	20 "	91
639-776 + H-156	10 "	12 "	21 "	88
639-776 + H-156 + 15% H-609	14 "	18 "	23 "	89
639-780	8 "	8 "	18 "	22
639-780 + RC-601	11 "	11 "	19 "	56
639-780 + H-156	14 "	11 "	20 "	64
639-780 + H-156 + 15% H-609	14 "	22 "	33 "	74
639-778	56 "	14 "	17 "	3
639-778 + RC-601	14 "	14 "	19 "	5
639-778 + H-156	14 "	22 "	21 "	24
639-778 + H-156 + 15% H-609	22 "	24 "	20 "	23

This increase in drying time of the alkyd whites, when doped with the ingredients comprising our universal vehicle, is most evident with the Triton X-100 addition, which of itself, has no drying potential. DCO, which slows the dry to some extent, is a semi-drying oil. To bring these drying times more in line, we feel that a drier combination should be incorporated into the color bases since the drier level in the white bases cannot be increased because of the skinning risk.

These dopings also gave us higher sag readings, in most cases from 2-3 mm., which in this range becomes significant. Where DCO and Triton were added to the Semi-Gloss, a reading of 33 mm. was noted. This is considered excessive. It should be kept in mind that the addition of any wetting agent to the alkyd whites will tend to deflocculate the system, causing an increase in sag. Although the above sag readings are indicative, actual tintings should be checked for more accurate results.

Finally, we checked the effect of the above dopings on the gloss of these products and a considerable increase for both the Semi-Gloss and Flat, when read initially against the controls, was evident. This initial increase in gloss, however, is not considered unusual and is noted whenever any of our standard shelf goods are tinted. Although the increase noted for Custom Color products is analogous to that found in our standard shelf goods, its magnitude could possibly result in flashing complaints, particularly with the Semi-Gloss and Flat. Since it is anticipated that for some time, the existing "632-Line" Colorants and the proposed Universal colorants will be used simultaneously in the field, some adjustment should be made to reduce the gloss differences noted.

Effect on Emulsion Viscosity:

In order to determine the effect on viscosity when 389-007 and 391-012 are tinted with our Universal Tinting Bases, tints were made at the 28/4 and 28/1 fl. oz. level with a W-527

and a W-895 grind in DCO at the 5% Triton level. No significant viscosity increase on tinting was noted either initially or on standing overnight with either 389-007 or 391-012. The maximum viscosity increase in these products was approximately 5-7 Krebs Units.

Stability:

A two month oven stability check of all pigments involved, dispersed in (DCO & Triton) were rated excellent for separation and settling resistance. Also, to date, there has been no indication that the ability of these bases to develop color has been impaired by either shelf or oven storage.

"39 Line" Dopings:

To determine if our present "39-Line" RC-601, soya/P.E., alkyd based colorants could be made compatible in the emulsion products, the following five ingredients were added to these bases both singly and in combination:

1. H-609, Triton X-100 at the 5% level
2. KH-5186, Kelsol at the 10% level
3. KH-5187, GMR at the 10% level
4. H-156, DCO at the 10% level
5. H-481, Tween 81 at the 10% level

These dopings were compatible to some extent in 389-007 and 391-012, the Kelsol doping giving the best results with inorganic pigmented bases and GMR giving the best results with organic pigmented bases. However, compatibility in the Sealer-Coater formulations was poor. A comparison of the relative compatibility of the doped "39-Line" bases vs. the (DCO + Triton) Universal Bases shows the latter to be far superior.

Competitive Universal Tinting Systems vs. Du Pont:

An evaluation of competitive universal tinting systems compared with Du Pont (DCO + Triton bases) is shown in the following table. It should be noted that no competitive system includes organic pigmented colorants.

	639-776	639-778	398-007	391-012	389-001	P-398- U- 94425
Sherwin-Williams	E	E	E	G	G	E
Pittsburgh Plate Glass	F	F	E	E	G	E
Archer-Daniels-Midland	F	E	G	E	NG	NG
Sears	NG	NG	F	F	F	F
Key Tint	E	E	E	G	P	G
Du Pont*	E	E	G	G	F	F

*Ratings for both organic and inorganic pigmented color bases with DCO and 5% Triton X-100 on the total base.

The compatibility rating of Key Tint in 389-001, PVA Sealer Coater does not correlate with the results obtained when examined previously. Compatibility at that time was rated excellent in 389-001.

Suggested Future Work:

1. Determine optimum Triton X-100 level for maximum compatibility.
2. Determine if H-632, Odorless Mineral Spirits, can be eliminated from our dispersions without impairing their universal tinting ability.
3. Develop a suitable grind of W-205, Lampblack, in (DCO + Triton)
4. Develop the composite pigmented bases, similar to the "632-Line" Custom Color Bases.
5. Develop extended color bases
6. Spot check blending of the color bases on an inter-mix basis.
7. Prepare cost data on final color base formulations.
8. Put out exposure study of Universal Tinting Bases in Two Purpose Outside White and Cement and Stucco White.

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test formulations)

Compatibility

Improvement in the compatibility ratings for these bases can be made, especially in the Sealer-Coater formulations, if the Triton X-100 level is increased.

Notebooks:

5495, 5828.

SALES DEVELOPMENT

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HRH:CWS:pc
12/7/54