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KV-45-80

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

Improvement of Flow of Lithol and "Duol" Reds

Period Covered: May 22, 1945 to September 5, 1945

FILE: 222.11

DATE: November 26, 1945

222.11

Serial N. KN-45-80

Copy No.

Copy to:

#1 - Numerical File
2 - Research Office (222.11)
3 - Library File (222.11)
4.- Imperial Chemical Industries, Ltd.
5 - " " " "
6-- " " " "
77 - D. H. Dawson, Newark Rec'd 12-14-45

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PIGMENT COLOR RESEARCH REPORT

Final Report

Title: Improvement of Flow of Lithol and "Duol" Reds

Period Covered: 5-22-45 to 9-5-45

SUBMITTED BY: A. D. Reidinger A D Reidinger DATE SUBMITTED: 10-18-45

APPROVED BY: A. A. Brizzolara A A Brizzolara 11/26/45 DATE ISSUED:

INTRODUCTION

In KN-44-84, a report was made of an evaluation of U.S. Patents 2,350,520-6 issued to Sherwin-Williams in June 1944. These cover improvements in ink properties of azo pigments and are of special interest in connection with the manufacture of Lithol Reds characterized by superior flow.

In the patents, considerable emphasis is given to the use of a rosin-maleic anhydride condensation product and the effectiveness of this compound in promoting flow in Lithol Reds was confirmed by the work covered in the report.

In view of the improvements in ink properties, resulting from the adduct, it was decided to investigate the use of maleic acid or other organic acids separately from the rosin, both being in the form of the sodium salts. Such a use, it is believed, would not infringe on the patents.

It was also proposed to attempt to match some of our standard Lithols and "Duols" with the added property of flow by introducing the rosin adduct into our own formulas and to figure approximate costs.

CONCLUSION

Use of maleic acid in the form of its sodium salt in conjunction with rosin but not combined as in the Sherwin-Williams patent example, was not successful in promoting flow in Lithol or "Duol" Red inks. It was necessary to prepare the adduct separately in order to obtain any advantage in ink properties. This was found to be the case both in the type of formula described in the patents and in our RT-464-D formula. A number of organic acids other than maleic were also found to be without effect when employed in a similar manner.

Modification of the RT-463-D formula by replacing the K Wood Rosin added after development with the rosin-maleic anhydride adduct resulted in products possessing excellent flow. However, in depth of masstone, finish and strength they resembled a "Duol" type rather than a Lithol Red. Because of the greater solubility of its barium salt, it was necessary to increase the amount of the adduct to equal the yield of toner obtained with wood rosin.

Substitution of the rosin-maleic anhydride combination for the wood rosin used in the development of the toner resulted in weak 'unturned' products.

By further modification of the RT-463-D formula, namely by increasing the amount of Wood Rosin in the development stage and by addition of rosin adduct after the development it was possible to approximate the depth and strength of RT-283-D with definite superiority in flow. A product closer tinctorially and also slightly cheaper was obtained by substituting the RT-283-D alkaline coupling for the acid type employed in the modification of RT-463-D described above.

As in RT-463-D, it was not possible to replace the rosin in the regular RT-283-D formula with the rosin-maleic anhydride compound. Complete substitution resulted in weak undeveloped products while partial (50%) replacement had

only a slight effect on tinctorial properties but also gave very little improvement in flow.

Flow was imparted to RT-364-D by replacing the blanc fixe and barium resinate added after development by rosin-maleic anhydride condensation product.

In the case of the calcium toners, RT-425-D, RT-432-D, and RT-464-D, it was not possible to obtain an improvement in flow without adverse effect on strength.

In view of the patent situation in respect to the use of the rosin adduct and the anticipated higher cost compared to wood rosin, work on this investigation was discontinued.

It is estimated that ingredients costs for the barium toners, RT283-D and RT364-D, in which the rosin-maleic anhydride compound was effective, would be increased by $2.11 and $1.32 respectively per 100 pounds of product.

SUMMARY AND DISCUSSION

As indicated above the RT-463-D formula was particularly adopted to treatment since the second addition of rosin (about 40% of the total amount) is made chiefly for the purpose of dilution and can be replaced by equivalent weights of other ingredients.

The lack of any effect on flow when maleic acid and rosin, as sodium salts, were added separately at this point is due in part to the solubility of the barium maleate formed in the color. Although used in much greater than equivalent amounts, no precipitation as its Barium salt occurred probably because of the high temperature and relatively high dilution of the strike volume. The low yields obtained in separate preparation of barium maleate confirmed this supposition.

Similarly, the solubility of other organic acids as their barium salts is sufficient to prevent precipitation. Among those tried were adipic, citric, tartaric, and benzoic acids. A slight improvement in ink body was effected by precipitation of benzoic acid as its aluminum salt which is much less soluble. However, the improvement is not considered sufficient to be of interest especially in view of the cost of the treatment.

The following derivatives of benzoic acid were also tried without success- salicylic, anthranilic, o-chlor benzoic, p-isopropyl-benzoic, and o-benzoyl-benzoic acids.

In addition to these, oxalic, stearic, and linseed oil fatty acids were tried without effect on flow.

The solubility of the barium salt of the rosin-maleic anhydride condensation product is also greater than the corresponding rosin salt, necessitating an increase of about 50% in the amount of adduct used when substituted in the RT-463-D formula. With this amount yield was equal to that obtained with rosin and flow was definitely improved.

Other condensation products tried but not found to be useful in promoting flow were Petrex (∆ terpenene-maleic anhydride) Trimol 80(Linseed oil-maleic anhydride) styrene, indene and ethylene-maleic anhydride resins and also a rosin-sodium polysulfite mixture.

The degree of improvement in flow which can be obtained by use of the rosin-maleic anhydride adduct is of the order of 20 points (1 point= 0.1 inch) in 2 minutes. Tests were regularly made on rubout inks prepared in #1 transparent varnish but were also checked on the standard type flow plate using inks ground on a mill. No flow was observed in the case of the lithols and "Duols" reds which were worked with.

The product obtained by substituting the adduct for rosin in RT-463-D was darker, stronger and less bronzy than that standard. By increasing the K Wood Rosin in the development by 40%, a typical "Duol" was obtained. Compared to RT-283-D, this product was more intense but transparent in masstone and definitely yellow in tint. This difference was reduced to a considerable extent by following the RT-283-D alkaline type coupling procedure.

As stated in Conclusions, the calcium lithols and "Duols" did not respond to treatment as did the barium toners. In the case of RT-464-D and RT-432-D a slight increase in flow was effected by after treatment with the rosin adduct but it was accompanied by a 15% loss in tinting strength, the improvement is not considered of practical interest. RT-425-D suffered a loss in strength without corresponding increase in flow.

Preparation of the rosin-maleic anhydride condensation product was made by simple fusion at 150°C. of a mixture of the two ingredients in powdered form. In the present work the stoichiometric ratio, of approximately 3 parts of rosin and 1 part of maleic anhydride was used. However, in the example of the Sherwin-William patent a ratio of 6.8:1 is employed. On a commercial scale the fusion could probably be made in a varnish kettle. Ingredient cost of the compound is calculated to be $0.10 with a possible total making cost of $0.20.

Costs of products in which this resin is used would therefore be higher than with wood rosin. For example:

	Ingredient cost	Flow
Exp. 548-35-D	25.84	17
RT-283-D	23.73	0
Exp. 548-4)C	30.10	13
RT-364-D	28.78	0

EXPERIMENTAL DETAIL

See Notebook 548.
A list of experiments made is tabulated below;

RT-463-D

548-14	K-2103. To check standard
13	" Rosin-maleic anhydride adduct replacing K Resin
15	K-2043. To check standard
16	K-2043. Rosin-maleic anhydride adduct replacing K Resin
17	Variation in amount of resin adduct added after development. K-2043 type formula
29	Variation in final pH of formula using adduct
19	Use of maleic anhydride as sodium maleate. Also phthalaic anhydride, naphthenic acid and sodium sulphate.
24	Increase amount of sodium maleate
26	Citric, tartaric, benzoic acids used in after treatment
27	Linseed fatty acids, trimol 80 " " " "
31	Derivatives of benzoic acid " " " "
33	Use of other metallic salts to precipitate rosin adduct. Also Petrex, oxalic, and Stearic acids
34	Increase in amount of benzoic acid
36	Increase in amount of Petrex
37	Styrene, indene and ethylene maleic anhydride resin. Also rosin-sodium polypulfite mixture.

RT-283-D

548-20	K-9595. Maleic anhydride rosin adduct and sodium maleate replacing K Wood Rosin
30	Increase K Wood Resin in 17C. formula to match RT-283-D
32	Continuation of 548-40
35	17C formula modified by use of alkaline coupling

Miscellaneous Lithols and Duols

548-38	RT-464-D Maleic anhydride-rosin and maleic anhydride naphthenic acid adducts replacing para soap and naphthenic acid.
41	RT-464-D addition of M.A. rosin adduct to strong RT-464-D
39	RT-425-D. Substitute rosin adduct for K-Wood Rosin
40	RT-364-D. Substitute rosin adduct for blanc-fixe and barium rosinate
42	RT-432-D. Substitute rosin adduct for B Wood Rosin. Also add in after treatment.
23	U.S. 2,350,520 example. Separate addition of sodium maleate and sodium rosinate
25	Recheck 548-23