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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT
Final Report

LITHOL RUBINE TONERS AND LAKES.

Period Covered: January - July, 1944.

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NEWARK PLANT

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Final Report

Title: LITHOL RUBINE TONERS AND LAKES.

Period Covered: January - July, 1944.

SUBMITTED BY: M. G. Taber
M. G. Taber

DATE SUBMITTED: 7-18-44

APPROVED BY: J. H. Cooper
J H Cooper 8/24/44

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INTRODUCTION:

The practicability of employing a direct laking process (i.e. one involving simultaneous coupling and laking) has already been demonstrated in the case of "Duol" Carmine. Previous work led to the development of a laboratory process (K-1552) for the orthodox pigment by this procedure and also resulted in the establishment of a formula for a darker, bluer product (K-1669) containing Tobias Acid as an accessory agent (c.f. Reports KN-42-35 and KN-42-82).

Aside from the obvious simplification in the number of operations of the new direct-laking process in comparison with the established orthodox procedure (which involved prior coupling of the dye and isolation thereof as the Sodium Salt), it is important to note that the new procedure rendered possible manufacture in more concentrated solutions, thus further decreasing manufacturing costs. The present study was undertaken to determine if further cost reduction is possible, and particularly to ascertain if commercial hydrated lime (the cheapest available alkali) could be employed as a substitute for both the caustic soda and the calcium chloride of the earlier K-1552 process. In a concurrent study of Calcium Lithols, the practicability of the "lime process" has already been demonstrated (c.f.K-2041).

SUMMARY AND CONCLUSIONS:

K-1552 represents the first "Duol" Carmine toner prepared by a direct laking process (KN-42-35). K-1994 introduces yet further simplification by employing hydrated lime in place of both caustic soda and calcium chloride. (Slaked lime costs less than one fifth the combined cost of the equivalent amounts of sodium hydroxide and calcium chloride). In K-1994 sodium acetate was omitted entirely and the rosin content increased over that in K-1552 without any sacrifice of strength. By rubout evaluation K-1994 is decidedly stronger than either RT-443-D or K-1552. Unfortunately, K-1994 has a very high oil wetting time, is bulkier than standard RT-443-D and dusts rather badly. To eliminate these defects K-2039 was developed. It contains 6% of Resinous Oil X-1* as a wetting agent. K-2039 equals standard RT-443-D in wetting time and degree of dusting. Tinctorially it is slightly darker than standard in masstone and equal in ultimate strength (stronger by rubout evaluation). Goal yields compare as follows:

K-1552, 590 lbs.
K-1994, 558 lbs.
K-2039, 614 lbs.

Against K-2039 Standard Ultramarine's Virginia Red CR-6500 is poorer in texture, and in rate of strength development, but is equal at ultimate strength. Its wetting time is substantially lower. Harmon's R-84 Lithol Rubine is superior to K-2039 in rate of strength development, nearly equal in texture.

*Manufactured by the Neville Company, Pittsburgh Pa.

Complete paint and ink evaluations of K-1994, K-2039 and K-2040 are in progress, and these reports should be consulted for further details.

K-1669 represents the first dark blue "Duol" Carmine developed using a direct laking process (KN-42-82). K-2040 has been developed using the new "hydrated lime" process. Like K-2039, K-2040 contains Resinous Oil X-1 to reduce bulk and wetting time. K-2040 has a darker masstone than K-1669 and is about 10% weak by rubout evaluation. It is very dark and blue versus RT-443-D and nearly equal in strength. Goal yield of K-2040 is higher because of high rosin content; for K-1669, 593 lbs.; for K-2040, 649 lbs.

K-2013 was developed as an improved RE-526-D. It is a lake of K-1994 on barytes. K-2013 by rubout evaluation is stronger (85p $\cong$ 100 p) than standard RE-526-D, but has no strength advantage by linoleum tests.

K-2017, a lake of K-2040 (without Resinous Oil X-1), is dark in masstone and blue in tint versus K-2013. Strengths are equal, both by rubout tests and linoleum tests.

A close match to RM-237-D (an extended non-rosinated calcium Rubine BG lake) could not be prepared by the hydrated lime-direct laking procedure, as too dark a masstone was obtained. The results did suggest, however, that a non-rosinated toner of some interest tinctorially might be obtained by this method. The entirely non-rosinated toner was far superior to any toner ever prepared from the sodium dye, but was weak and rather dull versus "Duol" Carmine and competitive low-rosinated toners. Small amounts of rosin noticeably increased both depth and strength. K-2033 contains only 3% of rosin. Compared with RT-443-D, it is very light in masstone, nearly equal in strength, but dull in tint. It has the oil absorption characteristics and bronze of a typical non-rosinated toner. In strength and depth of masstone it approximates some competitive Lithol Rubine toners, being fairly close tinctorially to Sherwin-Williams' Rubanox Red RG-C.P. 810, O#44520. Goal yield of K-2033 is 450 lbs./mol.

Color	Cost Yield 1 Br. Far Lb.*	R. M. Cost	Oil Wetting time	Std. for Comparison	Texture	MT	Rate of strength development	Ultimate strength	Strength by rubout	Strength in linoleum	Remarks
RT-443-D (SD-48028)	640*	59.32	7-8'	-							
K-1552	590	54.27		RT-443-D		light	better	st(92=100)	wk(105=100)		
K-1994	558		12-18'	RT-443-D	vs worse	s.light	better	st(92=100)	st(90=100)		
				K-1552		dark		equal	st(80=100)		
K-2039	614	50.02	7-8'	RT-443-D	vs worse	s.dark	better	st(92=100)	st(95=100)		
				K-1552		dark			st(90=100)		
				K-1994	vvs worse	dark	equal	equal	wk(108=100)		
			Va.Red 3-4'	Va.Red #6500	better	dark	better	equal			
K-1669	593		5-6'	RT-443-D		dark, blue	better		vs st.		
K-2040	649	47.60	8-9'	RT-443-D	worse	dark, blue	better	equal	equal		
				K-1669		dark	equal	wk	wk		
				K-2039	vs worse	dark, blue	equal	s.wk.	vs wk.		
RE-526-D	2740			-							
K-2012	2400			RE-526-D		vvs dk			st(85=100)	equal	
K-2017	2234			RE-526-D		dark, blue			st(85=100)	equal	
				K-2013		dark, blue			equal	equal	
K-2033	450			RT-443-D		light, bronzy			vs wk		
				C#44520		vs light			s wk		poorer l.fastness
				RM-237-D		dark			st.		

*100% dye basis

DISCUSSION OF RESULTS:

The major portion of the experimental work covered by this report was done in the development of K-1994 and K-2039. The results of variable studies, however, apply to the other formulas as well, unless otherwise stated.

EFFECT OF OPERATING VARIABLES:

1. pH - The proper amounts of lime must be present before coupling; for, unlike RT-443-D and K-1552, adjustment of pH after coupling has very little effect.

   Yield and strength are dependent upon the pH. Below a pH of 8 (measured after coupling) the rate of coupling becomes progressively slower and yields decrease rapidly, but strength within the pH range 7-8 is at a maximum. In the pH range from 9.5-10.5 yield is good and strength satisfactory. Much above pH 10.5 the strength drops rapidly. In the pH range 9-10.5, no buffer is necessary.

   Purity of hydrated lime is not easily determined and varies not only from lot to lot but from bag to bag. For this reason pH control of the lime-PTMSA solution and of the lime-BON slurry is necessary. In both cases uniform dispersion is required before accurate pH measurements can be obtained.

   The pH of the PTMSA-lime solution is the less important of the two in determining the pH after coupling, but it is a better guide to the purity of the lime. The formula amount of lime should give a slightly turbid solution with a pH about 8.

   The PTMSA will dissolve in slightly less lime to an almost clear solution of pH below 7, while slightly more lime gives a solution turbid with undissolved $Ca(OH)_2$ and a pH above 10.

   For a pH of 10-11 after coupling the diluted BON slurry should be adjusted to pH 10.8-11.0. For a pH after coupling of 9-9.5, the BON slurry should have a pH of 10.4-10.5. BON and lime form, before dilution, a thick, uniform, cream colored slurry. Adding the BON to a lime slurry gave more finely divided particles of the Ca salt than the reverse procedure. No heating was necessary.

2. Rosin - In every case, the K Wood grade of rosin gave the most satisfactory results. K-2039 contains slightly more calcium rosinate than K-1552, whereas K-2040 contains considerably more. Increasing the rosin content above the formula amounts will give darker masstone but loss in strength.

   For K-2033, additional rosin up to 12% of the pigment will give markedly increased strength and intensity, but with undesired increase in masstone depth. However, with a rosin content as high as 12%, the pigment is still very light and strong versus RT-443-D.

3. Volume - The coupling volumes of K-2039 and K-2040 are from 15-20% lower than those of K-1552 and K-1669 and very much lower than the volume of RT-443-D, standard. Decreasing the volume further, especially at higher pH's, causes noticeable loss in strength. Increasing the volume is of little benefit.

4. Temperature - Optimum strength is obtained for all the pigments, at the lowest practicable coupling temperatures. Below 77-86°F the rate of coupling becomes too slow. Above 95-104°F the tinctorial properties, especially strength, are harmed.

Development is desirable in all cases. Undeveloped pigments were light and weak. K-2033 required a higher development temperature (195°F) than the resinated toners (160°F). The slight increase in strength obtained for the latter at temperatures higher than 160-165°F. would not justify the cost of additional steam that would be required.

5. Wetting Agents - In an effort to reduce the high wetting times of the K-1994 type of pigment, a large number of agents were tested. They include abietyl alcohol, H.T.P. alcohols, zinc stearate, glyceryl monostearate, mannitan laurate, linseed oil fatty acids, naphthenic acid, Igepal CA, Alkanol B, and Resinous Oil X-1. This group includes representatives of most of the general classes of surface active agents. Most of these agents had a slight beneficial effect in reducing wetting time but two of them, mannitan laurate and Resinous Oil X-1 were outstanding. The addition of 6-8% of these agents reduced the wetting times to that of RT-443-D. In addition they increased the yield significantly and did not have any deleterious effect on strength. Mannitan laurate was of further interest in that it resulted in a pigment of superior texture, whereas the Resinous Oil X-1 had a slightly adverse effect on texture. Resinous Oil X-1 on the other hand is extremely cheap and easily obtainable at this time, whereas Mannitan laurate is not.

Best results were obtained with Resinous Oil X-1 when it was added as an emulsion in a rosin soap solution just before development. Adding the emulsion after development was not as effective. Satisfactory results were not obtained by substituting part of the oil for resin before coupling.

6. Accessory Agents - K-2040 and K-2017 contain 20 mol % Tobias Acid in place of PTMSA. This amount can be varied considerably with corresponding changes in tinctorial properties. As little as 2% Tobias Acid will deepen the masstone of K-2039 considerably and give a decidedly blue tint. Should it be necessary to use an accessory agent to deepen the masstone without affecting the tint, para-nitro-ortho-toluidine is more satisfactory.

7. Grade of PTMSA - Several grades of para-toluidine-meta-sulfonic acid were tested on the K-2039 formula. Material as low as 94% purity gave a good pigment without necessitating filtration of the initial

dark PTMSA-lime slurry before diazotizing. However, a very crude grade containing only 66% of PTMSA was wholly unsatisfactory, yielding a pigment dark, dull, and weak. Filtration of the PTMSA-lime solution did not help. In this case, the impurities in the crude intermediate had a marked effect on the pH of the coupling. With suitable pH adjustments at the crucial points it is probable that this intermediate too could have been used to make satisfactory pigment.

EXPERIMENTAL DETAILS:

For previous work on the direct laking of "Duol" Carmine see reports covering the development of K-1552 (KN-42-35) and of K-1669 (KN-42-82).

For the experimental work covered by this report refer to

N.B. 983 Experiments 18-41
N.B. 1098 Experiments 1-7, 10, 11, 13, 15-20, 22, 25, 28 & 30.