KN-63-3 RT-816-D - STRONG RHODAMINE Y By: R. F. White 2/61-12/62

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TECHNICAL SECTION - COLORS

NEWARK PLANT

PIGMENT COLOR FINAL REPORT

SUBJECT: RT-816-D - STRONG RHODAMINE Y

PERIOD COVERED: FEBRUARY 1961 - DECEMBER 1962

CHARGE: 5665-924

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SUBMITTED BY: R. F. WHITE R.F.W.hk DATE: 1/8/63

APPROVED BY: R. A. HAGEMAN R.A. Hageman DATE: 1-28-63

ABSTRACT

A high strength SMA Rhodamine Y product, RT-816-D, has been developed, standardized and released to the trade.

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INTRODUCTION

Some years ago Newark made a line of Basic Dye pigments (red, blue, violet, green, etc.). Competition in the field was strong, and as a result of low return, most of the line was "obsoleted" or cut to a minimum. However, the blue SMA (BT-264-D, Victoria BO) continued to grow because of its outstanding properties. This growth prompted the plant to install new and larger manufacturing equipment. These equipment modifications made possible larger batch sizes and other operating savings and resulted in a more attractive economic picture.

In 1961, two competitive Rhodamine pigments offered a serious threat to our remaining RT-612-D (Rhodamine Y) business. The competitives were Uhlich's Rhodamine Y and Collway's Rose Toner (R-4572). Of the two, the Collway product was considered better, being stronger and bluer than our offering. Sales requested the development (Product Development Request No. 24-1) of a counteroffering with the strength of the competitive and the good lightfastness of RT-612-D. Because of the improved economics, a study was opened.

Shortly after the PDR was issued, Sales surveyed the industry to determine exactly what was desired in a Rhodamine product. It became apparent that the trade was more interested in cost reduction through greater strength and were willing to sacrifice lightfastness to obtain it.

New samples of high strength products were obtained; and the best of these, a Collway PTA Rhodamine Rose Toner (R-4580) obtained at IPI, Elizabeth, was set up as the revised aim of the study.

SUMMARY & CONCLUSIONS:

1. A high strength SMA, Rhodamine Y product, RT-816-D, has been developed. This product is slightly stronger (3%), bluer, and more intense in tint with equal lightfastness compared to the best PMA competitive available (Collway's 4580). It is also slightly superior to the C# in ink mill characteristics, fluid ink uses, printing, solvent and paraffin bleeds, and has better drying characteristics. RT-816-D is about 40% strong, blue and intense versus RT-612-D.

2. Attempts to modify the RT-612-D PTMA formulation to prepare a stronger, bluer product were unsuccessful. However, trials using an imported dye (3GO) yielded a product that was about 25% stronger and blue versus RT-612-D.

3. A survey of plant RT-612-D production showed it to be stable throughout manufacture, and attempts to improve strength by alternate drying methods (spray dry) were unsuccessul.

4. Attempts to prepare a Rhodamine product via an SMA and a PMA route both yielded products equal to the competitive (Collway's 4580) in strength. However, the SMA route consistently gave a better overall product.

PATENT STATUS

There is nothing included in this study that is of a patentable nature.

DISCUSSION

Investigation - Laboratory

Initial study was aimed at upgrading RT-612-D to the level of the Collway and Uhlich products.

Varnish Drier Rubout

	Masstone	DD	Strength	Tint
RT-612-D vs. Collway's R-4572	dark,blue	yel	117=100	yellow,dull

Chemical analysis of the competitives showed both to be the PTMA type similar to RT-612-D. Infrared curves showed they contained Rhodamine 5GDN dye with possible trace amounts of Auramine and/or Rhodamine B. Orchem dye analysis confirmed these findings. The following table shows the chemical analysis of these competitives:

Sample	% W	% Mo	% P	% Si	DPG	B/F
RT-612-D, SD-91164	44.23	7.53	1.07	none	trace	none
C#58291, Collway's R-4572	40.93	7.50	1.19	none	trace	none
C#58292, Uhlich's Rhodamine Y	37.48	7.05	1.89	none	none	none

In addition, the Uhlich sample contained a fair amount of an agent that was organic in nature.

Based on the above analysis, several laboratory runs were made modifying the RT-612-D process. Some of the modifications yielded products that were superior to standard RT-612-D; however, none approached Collway's R-4572 in strength, intensity or blueness of tint. Some of these trials and their results are tabulated below.

Investigate Higher Dye to Hetro-Poly Ratio

All attempts to increase the dye in the standard RT-612-D formula yielded excessively weak products. All strikes except the control showed a very bad bleed during filtration and washing; indicating that under standard RT-612-D manufacturing conditions (acidity, heat development, etc.), it was not possible to form a complete and/or stable complex at higher dye ratios.

Evaluate Spray Drying & Survey In-Process Strength Relationships

Popular PTMA technology states that RT-612-D loses considerable strength (±10%) on pulverization. If true, eliminating the pulverization should increase the strength of RT-612-D by approximately one-half that required to match the competitive. To evaluate this, a sample of washed plant presscake was re-slurried and dried in the Bowen Laboratory Spray Drier. Rubout evaluation of this spray dried material showed that it was equal in strength to the plant tray-dried, pulverized control. These results re-opened the question of the suspected in-process strength loss. To check this, samples were taken from several plant RT-612-D lots. When compared by rubout, these samples showed no strength loss between plant lump and final grind, and less than 5% total strength loss from vat flushout to finished product. Consequently, no further attempts at alternate means of drying were made.

Define Variables Controlling RT-612-D Production

To define what factors control the complexing of hetro-poly acids and basic dyes, a survey was made of the formulae used in the development of the RT-612-D. These formulae, RT-329-D and RT-357-D, showed that higher strike and development temperatures were used and that the acid concentration of poly-acid could affect final strength.

To evaluate these variables, a 3 X 3 factorial design experiment was set up and a one-half replicate run. The main effects were considered at 3 levels and included:

(A)	Strike Temperature	120°F., 160°F., 212°F.
(B)	Acid Concentration	RT-612-D level, -10%, -20%
(C)	Phosphate Content	-10, RT-612-D level, +10%

All other variables were held constant.

Statistical analyses of these experiments showed that, at the 6:18 dye to poly-acid ratio used, the most important variable was strike and development temperature. Striking at the boil, gave the most strength. Acid concentration also was significant--lower concentrations giving more strength. The only other significant result was the first order interaction between temperature and acid concentration. Although these process modifications gave additional strength, none of the products approached the competitive in strength, intensity or blueness.

Evaluate 3-GO Dye

Previous tests and analytical data showed that if more strength were to be gained, the type of basic dye probably would have to be changed. Orchem was contacted (H. Stryker) and the problem reviewed. Their recommendation was that a 3-GO type dye might give us more strength and blueness.

A sample of this imported dye, used by Orchem, was obtained and evaluated as a PTMA product on an RT-612-D process. Rubout showed that the 3-GO dye was not the answer. However, its strength and blueness coupled with its lower price (approximately $4.60/lb.) make it interesting enough to carry out further evaluations.

	Masstone	DD	Hiding	Strength	Tint
TSC #64-14C, PTMA ex. 3-GO vs. C#58291, Collway's R-4572	vs dk,vs yel,int	blue	trans	90=100	v blue

24 Hour Lightfastness

MT	DD	Tint
Equal	Better	Vs Better

Develop SMA or PMA Product

About this time, a Sales review of the Rhodamine pigment situation with the trade indicated that there was considerable interest in cost reduction through greater product strength. The trade stated they were willing to sacrifice lightfastness to obtain this strength, and they suggested we use Collway's R-4580 as target. Studies to prepare a stronger product were directed along two paths. The first was similar to an old SMA formula, RP-651-D, and the second like the current BT-264-D formula. Each route was evaluated as a PMA and an SMA. Evaluation of these lab trials versus the competitive, C#58704, Collway's R-4580, gave the following results by varnish drier rubout:

Type	Type Process	MT	DD	Str.	Tint	24 Hr L/F DD	24 Hr L/F Tint
SMA	RP-651-D(A)	lt,yel	red	95=100	v blue	=	=
PMA	RP-651-D(A)	lt,yel	yel	110=100	yellow	=	worse
SMA	BT-264-D(I)	lt,yel	red	97=100	blue	=	=
PMA	BT-264-D(I)	lt,yel	red	102=100	s blue,dull	=	worse

The two SMA processes above showed that each was somewhat undesirable from a cost standpoint. The RP-651-D process used hydrochloric acid (N-28-D) and had a high dilution which would restrict the batch size. The BT-264-D process employed a sizeable quantity of acetic acid to aid in solublizing the dye. In addition, the precipitation is carried out in a buffered medium and has a relatively high dilution restricting the batch size. Additional lab trials were made modifying each process in an attempt to improve its manufacturing cost. The trials were:

Experiment	Type	Form	Acid	Dilution
TSC#64-20(E)	SMA	RP-651-D	HCl	full
(G)	SMA	RP-651-D Mod.	H_2SO_4	full
(H)	SMA	RP-651-D Mod.	H_2SO_4	one-half
TSC#64-20(A)	SMA	BT-264-D	H_2SO_4 + HAc	full
(B)	SMA	BT-264-D	H_2SO_4 + HAc	one-half
(C)	SMA	BT-264-D Mod.	H_2SO_4	full
(D)	SMA	BT-264-D Mod.	H_2SO_4	one-half

By rubout, these samples gave the following results when compared to C#58704:

Sample	Masstone	DD	Strength	Tint	24 Hr. L/F Drawdown	24 Hr. L/F Tint
TSC#64-20E	lt,yel	blue	95=100	v blue	=	vs better
G	lt,yel	blue	93=100	v blue	=	vs better
H	lt,yel	blue	95=100	v blue	=	=
A	lt,yel	blue	97=100	v blue	=	vs worse
B	lt,yel	blue	102=100	v blue	vs better	worse
C	lt,yel	blue	95=100	v blue	=	=
D	lt,yel	blue	100=100	v blue	vs better	worse

These results show that 20C and 20G (duplicate samples) are the best. The process used included sulfuric acid and high dilution. A comparison of 20G versus 20H, and 20C versus 20D showed a slight advantage for full dilution over double concentration. Further evaluation of sample 20G and 20H showed them to be equal or slightly better than the C# in lightfastness, ink mill working properties, printing ink, edible fat, paraffin and solvent bleeds, and lithographic break tests.

Semi-Works Manufacture

Based on these data, a semi-works batch was prepared and evaluated. The batch, coded RT-816-D, lot 10467, handled without incident. Lot 10467 was compared by rubout versus the competitive (C#58704). Lot 10467 was split after drying; the portion identified as 10467 received no treatment, while 10467-1 had 2% DPG added during pulverization.

	Masstone	Drawdown	Str.	Tint
10467 vs C#	v lt	blue,int	95	blue
10467-1 vs C#	v lt	blue,s int	97	blue
64-20 vs C#	v lt	blue,s int	95	blue
RT-612-D SD vs C#	lt,dull	blue	135	yel
10467-1 vs 10467	vs lt,s int	=	102	vs dull
64-20 vs 10467	int	=	101	vs yel
64-20 vs 10467-1	vvs lt	=	98	s int

	Trans.	Finish	24 Hr. L/F Drawdown	24 Hr. L/F Tint
10467 vs C#	opaque	s low	=	vs better
10467-1 vs C#	opaque	s low	=	vs better
64-20 vs C#	opaque	s low	=	vs better
RT-612-D SD vs C#	vs opaque	s high	better	better
10467-1 vs 10467	=	=	=	=
64-20 vs 10467	=	=	=	=
64-20 vs 10467-1	=	=	=	=

Evaluation showed the semi-works batch equal to the laboratory control (TSC #64-20G), and the DPG treated portion not significantly different from either. However, these products were more opaque in masstone, and had a slightly poorer finish.

Consequently, additional laboratory study was opened to further study:

(1) Dye to Molybdate Ratio
(2) Acid Concentration
(3) Development Conditions (Time and Temperature)
(4) Shading Effect of Auramine

Auramine - Shading

Small amounts of Auramine in the order of 0.5, 1.0, and 1.5% were used to yellow the product to bring the hue into line with the competitive. The higher amount (1.5%) of Auramine used had little effect on hue of masstone or tint. However, its use resulted in a considerably duller masstone and somewhat weaker product.

Dye to Molybdate Ratio

Changes in dye ratio gave no improvement in masstone depth or transparency.

Acid Concentration

Changes in acid concentration in the hetro-poly acid gave no improvement in masstone depth or transparency.

Development Conditions

Development conditions (time and temperature) have a significant effect on masstone depth and transparency. Rubouts show that lower development temperature (140°F) gives darker, more transparent masstone, and poorer lightfastness. Medium temperatures (160°F) give products that approach the competitive in depth and transparency of masstone and have equivalent lightfastness. High temperatures (180°F) yield products with light, yellow, opaque masstone and slightly better lightfastness. The cross comparison within temperature ranges shows that the longer development times (30 min. vs. 15 min.) yield lighter, yellower, more opaque products. In strength and hue of tint, all the products appear to be insensitive to any of the changes. Tabulated below are the rubout results of this series versus the competitive (C#58704 - Collway's R-4580):

Sample	Time/Temp.	Masstone	Drawdown	Str.	Tint
64-27A vs C#	15/140°F	v dk,dull	blue,int	94	blue,int
B	30/140°F	v dk,dull	blue,int	94	blue,int
C	15/160°F	dk,dull	blue,int	94	blue,int
D	30/160°F	s dk,dull	blue,int	93	blue,int
E	15/180°F	lt,yel	blue,int	94	blue,int
64-25E	30/180°F	lt,yel	blue,int	93	blue,int
27B vs 27A	30/140°F	s lt			
	15/140°F	yel			
27D vs 27C	30/160°F	s lt			
	15/160°F	yel			
25E vs 27E	30/180°F	s lt			
	15/180°F	yel			

Sample	Time/Temp.	Trans.	Finish	24 Hr. L/F DD	Tint
64-27A vs C#	15/140°F	trans	less bronz	W	s W
B	30/140°F	trans	less bronz	W	vs W
C	15/160°F	s trans	=	vs W	vs W
D	30/160°F	vs trans	=	vs B	=
E	15/180°F	opaque	=	vs B	vs B
64-25E	30/180°F	v opaque	less bronz	vs B	s B
27B vs 27A	30/140°F				
	15/140°F	vs opaque			
27D vs 27C	30/160°F				
	15/160°F	s opaque			
25E vs 27E	30/180°F				
	15/180°F	opaque			

Based on these results, a second semi-works batch, lot 10472, was prepared using 30 minutes at 160°F. development. By varnish drier rubout, lot 10472 tested as follows versus the competitive, Collway's R-4580 (C#58704).

	MT	DD	STR	TINT	TRANS	24 Hr. L/F DD	TINT
Lot 10472 vs C#58704	dk	blue,int	93=100	blue,int	trans	vs B	=

A plant batch, lot 66789, was manufactured on a formula patterned after SW lot 10472. This formula, (A)RT-816-D, differed from the current BT-264-D(I) process as follows:

	RT-816-D	BT-264-D
Dye Solution	158-162°F water	170-175°F water + 19 moles of acetic acid
Dye to Poly-Acid Ratio	6:22	6:18
Acid	Sulfuric-55 moles	Sulfuric-51 moles
Silicate	4 moles	4 moles
Strike Temp.	158-162°F	183-187°F
Development	30 min.-158-162°F	15 min.-183-187°F
Strike Condition	Unbuffered	Buffered
Dilution (approx.)	10 gal/1 lb.	10 gal/1 lb.
% Blanc Fixe	2.2	2.4
% DPG	0	1.0

Results of this batch were satisfactory. Several other plant lots were struck and portions held for a possible standard. These lots were combined to form PS 96770-1.

Firm costs on the process indicated a return of about the same magnitude as BT-264-D (±14%).

Sales has released the product; and to date, it has been well received by the trade. In addition to high strength and acceptable lightfastness, the product has good drying characteristics, requiring less drier. This results in a distinct reduction in the objectionable odor associated with its use.

REFERENCES:

TSC #49-50
62-18
64-5, 7, 8, 9, 10, 12, 14, 19, 20, 22
SW 10467
SW 10472-1 & 2
RT-816-D, lot 66789-1

Memorandum: Discussion of Rhodamine Dyes - R.A.H., 6/1/61