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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

TOLUIDINE RED, MEDIUM SHADE: RT-620-D
LABORATORY AND PLANT DEVELOPMENT AND STANDARDIZATION
OF IMPROVED TOLUIDINE TONER

Period Covered: October 25, 1948 - March 15, 1949

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: Toluidine Red, Medium Shade: RT-620-D
Laboratory and Plant Development and Standardization of Improved Toluidine Toner

Period Covered: October 25, 1948 - March 15, 1949

Charge: 1101-11-44 (Lab. Development and Evaluation)
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SUBMITTED BY: Malcolm B. Ver Hoey

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INTRODUCTION

RT-620-D, toluidine red, was developed in an attempt to approximate an improved competitive toluidine toner, Harmon's RT-1 (C-51159), which is superior to the old standard RT-386-D in depth and intensity. Lot 89319 has been set up as the official standard for RT-620-D. It is lighter and more intense than RT-386-D, but on the dark side of RT-1.

SUMMARY

After a month's laboratory work, a process was taken into the plant on November 23, 1948, which forms the basis of the present formula. Eleven 1090# batches were made during November and December on this formula. A 500# mix was made from 100# each of five plant batches as the new standard (lot 89319). Since January 1, 1949, 17 more batches have been run satisfactorily on both the 1090# and 2180# batch size.

Meanwhile work continued in the laboratory toward further improvement in the color. Two variables, use of Setex C and excess sodium bicarbonate, look promising, but time did not permit their evaluation in plant development batches.

DISCUSSION

Against RT-1, RT-386-D appears definitely dark and dull. Investigation of all the old standards for RT-386-D from 1934 to date indicated that there was a gradual trend toward darkness and dullness, corresponding to the development of the economy formulas (HLM #48-38). However, none of these former standards could compare in both depth and intensity with RT-1.

A laboratory program was instituted to make the necessary changes in the process to give the desired depth and intensity. From four series of experiments on a 0.2 mol scale was derived a formula which gave a product equal to RT-1 in acetone. This formula was scaled up to a 3.6 pound-mol plant batch which was first made on November 23, 1948. The result was darker than the laboratory product and and RT-1, but approximately equal in intensity. It was superior to RT-386-D in lightness and intensity, but 10% weak and blue in tint. Of the total of ten batches made prior to January, 1949, five were similar to the first one. The other four suffered from effects of operating difficulties or variable studies.

The process used in these batches, coded (E) RT-386-D at first, then (A)RT-620-D, differs from the previous RT-386-D standard formula in the following respects:

1. The MNPT is slurried directly into the approximately 3.4N hydrochloric acid solution instead of in water.

2. The sodium nitrite excess is increased from 1-1/2 to 3%.

3. The BN is reduced from 529#, a 4% excess, to 522#, a 2% excess. It is reprecipitated from the caustic solution with acetic acid instead of with sulfuric acid.

4. The 190# soda ash is replaced with 148# (1.8 mol) sodium acetate. The 300# sodium bicarbonate remains unchanged. As a result considerable foam forms during first half of coupling. In the earlier formula the diazo acid is neutralized by the soda ash with the formation first of sodium bicarbonate, and foam does not build up until the end of the coupling. With no soda ash present, the pH drops rapidly and the bicarbonate is decomposed by the acid to form carbon dioxide

which produces the foaming. This foam breaks when about half the diazo has been consumed.

5. The pH drops quickly as the diazo is added to the BH slurry. The pH, with half the diazo added, is approximately 6.3. The final pH is around 5.3. The final pH of RT-386-D (B) is approximately 7.

6. The coupling temperature has been reduced from 111-113°F to 96-98°F.

Otherwise no more special techniques are required in the control of this process than in the RT-386-D formula. No changes are required in pressing, drying, grinding, or standardization. The cost penalty as a result of these changes in the process is approximately 2.6 cents a pound.

One hundred pounds from five of these batches were combined into a 500# mix to form the new standard. Since then twelve more 1090# batches have been run in the plant, eight of which were satisfactory. The other four were affected by variable studies on the process.

On six plant batches variables were run to determine their effect on the color. The variables were as follows:

1. Use of para soap. Five pounds para soap added prior to coupling had only a slight darkening effect on the color. Ten pounds gave a dark maastone with no loss in intensity but a slight decrease in strength.

2. Replacement of 300# sodium bicarbonate with 190# soda ash and 30# sodium bicarbonate. The use of soda ash in both plant and laboratory gave a lighter but duller product, 8 - 10% stronger and yellower in tint.

3. Lower coupling temperature. The present coupling temperature, 96 - 98°F, is as low as can be safely used, and cannot be lowered further. A 3° decrease in coupling temperature gave a lighter but duller product with no change in strength.

4. Use of lower coupling temperature and para soap. The intent was to compensate for the light, dull product at a coupling temperature of 90 - 92° with the darkening, brightening effect of 10# para soap. The result was dark and 2% strong and yellow.

5. Use of soda ash and a higher coupling temperature. The intent was to compensate for the light dull product produced by 190# soda ash with the darkening, intensifying effect of a 101-103° coupling temperature. In this case the higher coupling temperature was not a potent enough variable, and the product was still light, dull, 15% strong and yellow.

Meanwhile, other variables were being investigated in the laboratory. It was found that an increase in amount of sodium acetate would decrease depth and increase intensity, but a 1090# batch would require 147# more sodium acetate for any appreciable effect on the color.

An increase in the amount of hydrochloric acid used to slurry the MNPT in the beginning from 2.2 mol to 2.5 mol per mol of MNPT had a slight dulling effect on the color.

In the plant sodium acetate is made by combining the proper proportions of caustic soda and acetic acid in an iron vat. An attempt was made to eliminate this step by adding excess caustic when dissolving up the BN and reprecipitating the BN with excess acid; but this produced a duller product.

Replacement of sodium bicarbonate with varying amounts of soda ash from an equivalent to an equi-molar amount gave results similar to those in the plant- lighter but duller product. In fact, any experiment in which soda ash was used in any proportion gave a dull product.

Decrease in the concentration of the BN slurry had little effect.

A lengthy series was run utilizing different detergents and wetting agents, in 2% and 5% amounts based on pigment, which were added to the BN slurry before coupling or to the pigment slurry after coupling. The following treating agents were tried: Nulsor 30W, Nopcoset A, N, C; Sotex N, P, C, NC, CW; urea, para soap, Alkanol B. None of these gave any improvement in lightness and intensity in pre-coupling treatment. Only Sotex C was beneficial in post-coupling treatment, but has yet to be tried on a plant scale. It would increase the cost penalty considerably.

An increase in the amount of sodium bicarbonate used from one to 1.5 mols had a beneficial effect on the color. In fact, laboratory experiments seemed to indicate that the preparation and addition of sodium acetate could be eliminated in experiments involving excess sodium bicarbonate. It might even be possible to go back to a modified RT-386-D formula, in which soda ash was eliminated in favor of a 50% increase in sodium bicarbonate, and with a lower coupling temperature. The advantage of this would be that the present RT-620-D could be matched at a much less cost penalty than at present. These experiments have never been tried on a plant scale, but should be investigated.

The result of all this plant and laboratory investigation was a formula on which the plant could standardize, RT-620-D (C), which replaced (A) RT-620-D and differed from it in the following respects:

1) The BN has been increased 5# from 522# to 527# to insure against any possible diazo excess. A 4% excess, 529#, is used in the RT-386-D (B) process. Laboratory work showed that reduction in the BN to 522#, a 2% excess, gave somewhat better intensity, but this margin was too close for plant operation, and positive diazos resulted three times. Increase to 527# eliminated the difficulty with excess diazo.

2) The size of the orifice has been set at 9/32" throughout the coupling and the coupling time increased an hour to four hours in order to minimize the build-up of foam and eliminate the frequent stirring periods required to dissipate the foam. The three step coupling procedure, coupling rapidly for 35 minutes until foam was heavy, stirring over 20 minutes until the foam broke, and then slow coupling until the end, was carried over from the RT-386-D (B) process into the (A) RT-620-D process. This proved unsatisfactory in the new formula, and has been replaced by a better coupling procedure, which does not require constant supervision by an operator.

3) Sodium bicarbonate was increased from 300# to 330# in order to raise the final pH after coupling. The final pH with the (A) RT-620-D process was approximately 5.3.

The RT-620-D (B) formula is an alternate to RT-620-D (C) and is based on an increase in batch size from 1090# to 2180#.

The (B) and (C) formula were accepted by the plant on March 9, 1949.

REFERENCES:

Notebook 1217, Expts. 25-52
Notebook 1334, Expts. 2, 3
KN-49-14, 46-37
HLM-48-38
DSH-49-16