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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

Reactivity of "Naphthanil" Maroons

Period Covered: February 1946 to June 1946.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: Reactivity of "Naphthanil" Maroons.

Period Covered: February 1946 to June 1946.

SUBMITTED BY: F. KARUSH DATE SUBMITTED: 12-24-46

APPROVED BY: B. H. PERKINS DATE ISSUED: 1-6-47

INTRODUCTION

The reactivity of paint systems is a phenomenon which is frequently encountered and is of great practical importance. In the case of some pigments it becomes a decisive factor in determining their use in such systems. One group of pigments which shows sufficient reactivity to make it of primary concern is that known as the "Naphthanil" Maroons. The members of this group (eg. RT-501-D, RT-551-D) show varying degrees of reactivity, some to the extent that preclude their use in alkyd enamels.

The earlier studies of this problem were largely directed towards the practical goal of controlling the reactivity of specific pigments. These have not generally met with success and have yielded practically no insight into the physical and chemical changes associated with reactivity. The study which is described in this report was undertaken with a view to elucidating the processes involved in reactivity. It was considered possible that such fundamental information would serve to provide a more intelligent approach to the practical control of the reactivity of specific pigments. Because of the importance of this phenomenon for "Naphthanil" Maroons, as well as the importance of the pigments themselves, and because information was available from previous studies, the experimental work in this study was conducted with these pigments.

SUMMARY AND CONCLUSIONS

1. The reactivity of "Naphthanil" Maroons in alkyd enamels involves an essentially reversible increase in the apparent viscosity of these systems. The rate of this process increases rapidly with increase in temperature although the temperature coefficient may not be the same for all systems.

2. During this process the enamels develop a thixotropic structure. Under certain conditions, commonly encountered, this development will proceed to the point where the system does not flow under gravity (gelation).

3. Although only some of the enamels are Newtonian initially (viscosity independent of rate of shear), all can be made so by sufficient stirring. Furthermore, even after gelation has occurred, stirring can convert the system to a Newtonian one even though the value of the viscosity may be several-fold greater than the original figure.

4. The reactivity of the "Naphthanil" Maroons does not appear to involve significantly any irreversible chemical changes including, in particular, the polymerization of the vehicle.

5. The apparent viscosity of undisturbed aged enamels is very sensitive to mechanical disturbances such as stirring. This means that it is practically impossible to obtain a meaningful measure of

viscosity with any of the usual instruments, both because the system is constantly changing and because an experimental distinction between yield value and viscosity is not made. In further work along these lines it is suggested that an experimental technique be employed which will furnish a quantitative measure of thixotropy and yield value.

6. Spectrophotometric studies have revealed that the "Naphthanil" Maroons contain considerable quantities of non-colored impurities, to the extent in some cases of about 30%. However, these impurities have not been shown to affect reactivity either for better or for worse.

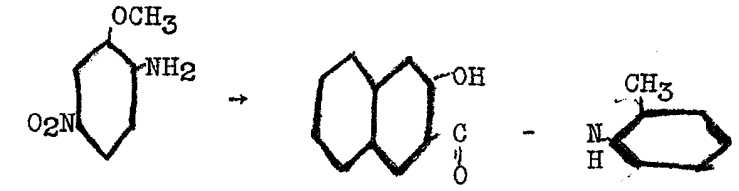
7. The attempt was made to determine the influence of the nature of the thinner on the reactivity of the enamel but clear-cut results were not obtained. It was observed, however, that substitution of 24% of the mineral spirits, the thinner generally employed, by other solvents, did significantly affect the viscosity of the enamel. This was most pronounced in the case of butanol, by the use of which a 5-fold reduction in the viscosity of the vehicle was noted and a 2-fold decrease in the viscosity of the enamel. The latter decrease was also carried over after aging had greatly increased the viscosities of the enamels under comparison.

8. Many factors are involved in determining the reactivity of an enamel. Aside from the relative proportions of the several components, the nature of the vehicle and thinner are important. As far as the pigment is concerned, its particle size and probably shape are important factors. Finally the structure and composition of the pigment surface as it exists in the dispersed system is of primary importance. This last factor is perhaps the one which is most feasibly controlled in the pigment synthesis.

9. The results of this study have not lead to any single means for the control of the reactivity of "Naphthanil" Maroons. Any further work of a fundamental nature should involve a study of the surface structure of the pigment and its bearing on reactivity. In addition it would be desirable to determine the importance of particle size using purified samples of the same chemical composition.

GENERAL DISCUSSION

In this study attention was directed towards two chemical types of "Naphthanil" Maroons. They result from the couplings of (1) 5-nitro-2-amino anisole with "Naphthanil" AS-D, and (2) p-chloro-o-nitro aniline with "Naphthanil" AS-D.



5-nitro-2-amino anisole

"Naphthanil" AS-D

RT-551-D

p-chlor-o-nitroaniline

"Naphthanil" AS-D

RT-500-D
RT-501-D

The alkaline coupling of the former type (1) is the basis for the manufacture of RT-551-D. In the latter case (2) the acid coupling gives RT-500-D and the alkaline coupling RT-501-D. Of these, RT-551-D and RT-501-D are regarded as presenting serious reactivity problems. Most of the experimental work was done with enamels prepared from these two pigments.

One of the characteristic properties of the enamels studied is the development of thixotropy on aging. This is manifested, for example, by the observation that the apparent viscosity of aged enamels continually decreases during measurement, and also by the fact that rapid stirring may cause a several-fold decrease in the apparent viscosity. Even when gelation has occurred on aging overnight at 120°F., rapid stirring can reverse the process and produce an enamel which flows readily. This reversibility can be carried almost to completion if sufficient mechanical work is done on the system. It is significant that the amount of work required to bring about a specified decrease in viscosity increases rapidly as the viscosity decreases. The importance of the thixotropic change in explaining the reactivity process is underlined further by the fact that even with an enamel containing only 2.5% pigment, a thixotropic structure develops. The reversibility of the process permits one to conclude that such irreversible chemical changes as the polymerization of the vehicle are not significantly involved in the reactivity of the enamels studied.

In attempting to explain the thixotropic behavior of these enamels in terms of the interaction between pigment and vehicle, it is useful to introduce the concept of order and to indicate how the degree of order in a system may affect its flow properties. This may be done simply by considering the fact that water can exist both as a liquid and as a solid at 0°C. The solid form is associated with the fact that the H_2O molecules are arranged in an ordered crystalline structure, whereas in the case of the liquid the geometrical relations of the H_2O molecules are much less fixed. Likewise in the case of thixotropic enamels it must be assumed that there is to some degree an ordered arrangement of the pigment particles. It may also be reasonably assumed that, depending on the degree of thixotropy and associated with the ordering of the pigment particles, there will be an ordering of at least a portion of the alkyd molecules of the vehicle.

The experimental results obtained in this study can be accounted for, at least qualitatively, by an interpretation of the reactivity process in terms of oriented adsorption of alkyd on the pigment surface. The oil-modified alkyd used in this study consists of long chain molecules composed of glyceryl-phthalate residues with the fatty acid chains bonded to the β-carbon atom of the glycerol residue. It appears necessary to assume that in the case of pigments which show reactivity that there is adsorption of alkyd molecules on the pigment surface, otherwise it would be expected that the pigment would settle out. This view is supported by the observation that in the enamel made with RT-436-D, which is non-reactive, the pigment does settle out to form a cake. Because of the polarity of the glycerol-phthalate residue and the length of the chain composed of these residues on the one hand, and the probable polarity of the pigment surface on the other, it is to be expected that the adsorption involves orientation of the alkyd molecules. This orientation would be such that the alkyd chain would lie flat on the crystal face and the fatty acid chains would be more or less perpendicular to the surface. Because of the fixed position and orientation of the first strongly adsorbed layer, further ordering beyond this layer would occur either in the sense of the formation of multi-layers or in the sense of extending the order into the liquid. The latter effect would be in some respects similar to the role played by crystalline nuclei in precipitation processes.

On the basis of the above picture the thixotropic structure would develop as the relative positions of an increasing proportion of the pigment particles and the alkyd became fixed. When the order had developed to the stage where it was continuous throughout the entire volume, the system could be regarded as gelled and would so behave. On stirring, the system would break down at the weakest points, i.e. where the bonds were few or the binding energy small, and form what might be called "gelates". These would be gelled structures similar to the original gel but much smaller in volume. The motion of these gelates would be more or less independent of each other depending on their number. It is then easily seen how after a certain amount of stirring the system could still show Newtonian behavior even though its viscosity had increased over the original value. This picture

then accounts for the experimental observations in which gelled enamels behaved as Newtonian systems although their viscosity after stirring was much greater than before aging. The increase of viscosity in the presence of "gelates" arises from the fact that the "gelate" immobilizes a portion of the liquid phase and brings about an increase in the effective volume fraction of solid.

The increasing resistance to viscosity change as stirring continues can be explained in terms of the size of the "gelates". At a given stirring speed the shearing stress to which a "gelate" is subject diminishes as its size decreases. At a certain size this stress will be insufficient to reduce further the "gelate" so that the viscosity will tend to remain constant.

SUMMARY OF EXPERIMENTAL DETAILS

1. Preparation of enamels.

The enamels used in this work were prepared by grinding in one pint jars for 85 hours on the roller mill the following quantities of material:

pigment	- 30.0 grams
vehicle (GE-2458 or Aroplaz 1320)	- 84.0 "
mineral spirits	- 36.0 "
steel shot	-600 "

The vehicle usually used was the alkyd GE-2458 except for a short period during which Aroplaz 1320 was used as a substitute. After the grinding period 150 grams of additional vehicle were added and the mixture ground for an additional 1/2 hour. The enamel was passed through a coarse cloth filter and usually placed in several 2 oz. bottles. No driers were added, to avoid skinning and other possible complications. The presence of drier does not seem to be a significant factor in the reactivity. Accelerated aging was ordinarily carried out in a 120°F. oven although in one experiment a temperature of 190°F. was used.

2. Viscosity measurement.

For the measurement of viscosity the Brookfield viscosimeter (Model LV-4 speed) was employed. This is a rotational type of instrument and is convenient because it permits the use of four speeds and four different spindles covering a range of viscosity in terms of full-scale deflection of 100 to 100,000 centipoises. Also the viscosity is read directly in absolute units of poises. Measurements were usually made with the guard removed and the spindle immersed in the 2 oz. jar containing the enamel. Under these circumstances a correction must be made before the deflection can be converted into absolute units. To avoid variations due to temperature fluctuations, all viscosity measurements

were made at constant temperature by immersing the jars to about 1/2 inch from the top in a constant temperature water bath maintained at 25.1°C.

Inasmuch as most of the enamels were gelled after aging overnight at 120°F., it was necessary to set up some standardized stirring procedure to obtain meaningful values of viscosity. It was found most useful to stir the enamel for 5 minutes in the bath with a high speed "Lightning" stirrer. This was sufficient to convert the enamel to a Newtonian system but not to eliminate completely the effect of aging. The Newtonian character of the enamels was ascertained by making viscosity determinations at several speeds.

3. Reversal of aging.

The reversal of the aging process insofar as viscosity increase is concerned can be illustrated by an enamel of RT-551-D (1205-9C2) containing 5% pigment. This had an initial viscosity of 4.06 poises and after 3 hrs. at 190°F. had gelled. Stirring for five minutes destroyed the gel structure and gave a Newtonian system with a viscosity of 8.4 poises. Five minutes additional stirring further reduced the viscosity only slightly to a value of 7.7 poises. The enamel was then ground on a jar rolling mill with steel shot for 3 days. This led to a further reduction of viscosity with a value of 5.2 poises. These results show that after considerable aging the enamel can be brought back almost to its original state, as far as viscosity is concerned, if sufficient mechanical work is done on it.

4. Rate of viscosity increase.

To determine the rate at which the systems change on aging, enamels were prepared from RT-501-D (lot 6253) and RT-551-D (lot 8338). These were made using GE-2458 as the vehicle and contained 10% of pigment by weight. Viscosities were determined after 4 hour aging intervals, as well as 16 hour intervals at 120°F. The measurements were preceded by the usual 5 minute stirring period. In addition to the study of the enamels, parallel measurements were made on an unpigmented control to observe the effect of elevated temperature (120°F) on the vehicle itself.

The results are presented in the graph of Fig. 1 where viscosity in poises is plotted against aging time in hours. In the first place it should be noted that whereas the initial viscosity of the vehicle is 1.56 poises, that of the RT-551-D enamel is 3.68 poises and of the RT-501-D enamel 7.8 poises. The difference in the last two values suggests that the RT-501-D has reacted in the grind. Both enamels show the characteristic rapid initial rise in viscosity and the slow linear increase beyond this. It is also of interest to note that the RT-501-D enamel develops considerable thixotropic structure on standing overnight at room temperature whereas the RT-551-D enamel does not. The effect of aging, for the period here involved, on the viscosity of the vehicle alone is seen to be slight.

5. Thixotropy of 2.5% enamel

In order to study the thixotropic behavior of a system of low pigmentation, an enamel made with GE-2458 and containing 10% of RT-551-D (lot 8338) was diluted with the appropriate combination of thinner and vehicle to give a 2.5% enamel. The combination was such as to maintain the ratio of alkyd to thinner constant. The enamel was then aged at 120°F. for successive periods of 17, 19, 21, 22 and 65 hrs. to a total of 144 hrs. Viscosity measurements were made after each period both before and after the standard stirring procedure.

The data are summarized in Fig. 2 where viscosity in poises is plotted against total aging time. Two values for the viscosity are indicated at each of the several total aging periods, the upper set representing the measurement made before stirring and the lower set those after stirring. The latter are connected by a smooth curve which shows the familiar rapid initial rise in viscosity and then the slow linear increase. The former do not represent stable viscosities because even the relatively slight stirring involved in the measurement caused a continuous decrease in the reading. The data clearly reveal that even at this low pigmentation a thixotropic structure develops.

6. Effect of addition of NAS-D.

Because of the presence of "Naphthanil" AS-D as an impurity in both RT-501-D and RT-551-D an experiment was carried out to determine its role in affecting reactivity. 10% enamels of RT-551-D (lot 27914) were prepared with Aroplaz 1320 to which were added 0, 10 and 20% of "Naphthanil" AS-D on a pigment basis. The enamels were aged at 120°F. for a total of 184 hours with viscosity determinations being carried out at intervals. No significant differences were found among the three systems. Attempts to determine the reactivity of purified samples of the pigments were unsuccessful because of the difficulty in removing more than a fraction of the impurities.

7. Effect of thinner.

On the basis of the fact that the viscosity of alkyd solutions varies considerably with the solvent employed, it was decided to evaluate the effect of the nature of the thinner on the reactivity. Enamels were prepared containing 10% of RT-551-D (lot 8338) and GE-2458 with the substitution of 24% of the total mineral spirits by several thinners. The enamels were aged at 120°F. and viscosities determined before and after aging. Table I below lists the substitute thinners and relative viscosities of the corresponding enamels both initially and after 64 hours at 120°F.

TABLE I.
Effect of Thinner

Thinner	Initial	64 hrs.
Mineral Spirits	16.8	46.1
Solvessol #2	10.4	29.6
Hexane	17.4	43.4
Toluene	11.1	25.2
Butanol	7.4	22.7

A value of the relative viscosity of 10 corresponds to an actual viscosity of 2.25 poises. It is clear that the viscosity both before and after aging is very sensitive to the kind of substituted thinner. The lowest values are obtained with butanol, probably because of its polar character.

8. Purity of "Naphthanil" Maroons.

In connection with the possible role of impurities as a factor in reactivity, spectrophotometric studies were made of several maroons. It was found possible to determine the purity of a particular maroon by comparing its absorption with that of a purified sample. Purity determinations were made in this way for RT-500-D, RT-501-D and RT-551-D. Since the first two pigments are made from the same components a purified sample of RT-501-D, assumed to be of 100% purity, was used as the standard for them. For RT-551-D a purified sample of the pigment was employed.

The absorption spectra of purified RT-501-D and purified RT-551-D in solution are given in Figs. 3 and 4 respectively. They consist of a plot of optical density versus wave-length for the range of 320 millimicrons to 680 millimicrons. The absorption was measured with the Beckman Spectrophotometer at a concentration of 2.00 mg/100 cc chloroform with a cell length of 1 cm. In the case of RT-501-D the absorption maximum occurs at a wavelength of 525 millimicrons and with RT-551-D at 550 millimicrons. Since the impurities do not absorb significantly in the region of maximum absorption, the purity of a sample could be obtained directly from the ratio of its optical density to that of the standard at the wavelength of maximum absorption. In this way the purities of the three pigments were determined with the following results:

Pigment	Purity
RT-500-D (SD-48035)	88.5%
RT-501-D (lot 6255)	72.2%
RT-551-D (lot 8538)	82.5%

Though these pigments contain considerable impurities as the above results indicate, it has not been possible to determine to what extent they influence the reactivity of the pigments.

REFERENCES:

1. Viscosity studies - NB-1205.
2. Spectrophotometric studies - NB-1011, Expts. 31, 32.

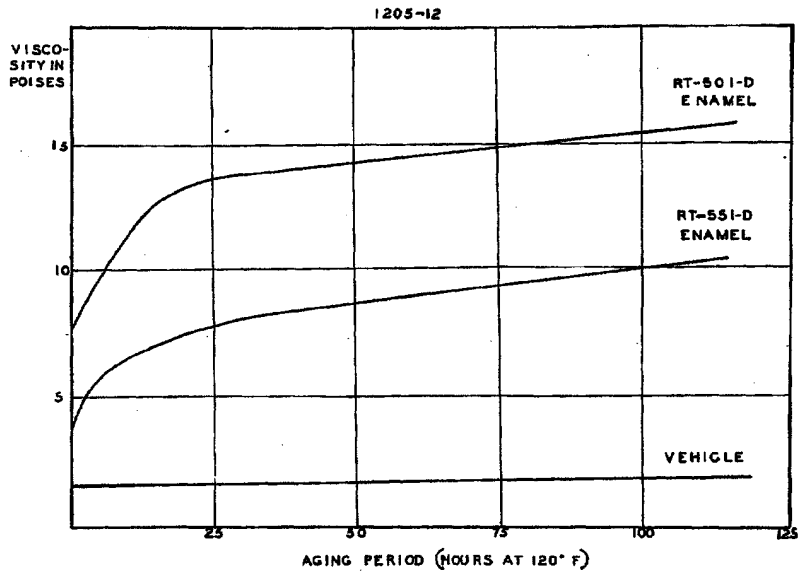


FIG. 1 - RATE OF AGING AT 120°F.

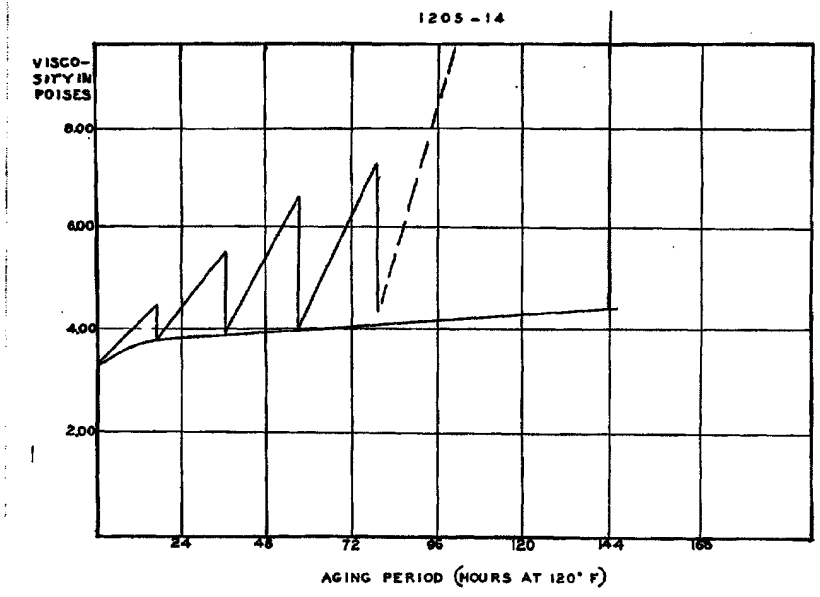


FIG. 2 - AGING OF 2.5% ENAMEL (RT-551-D)

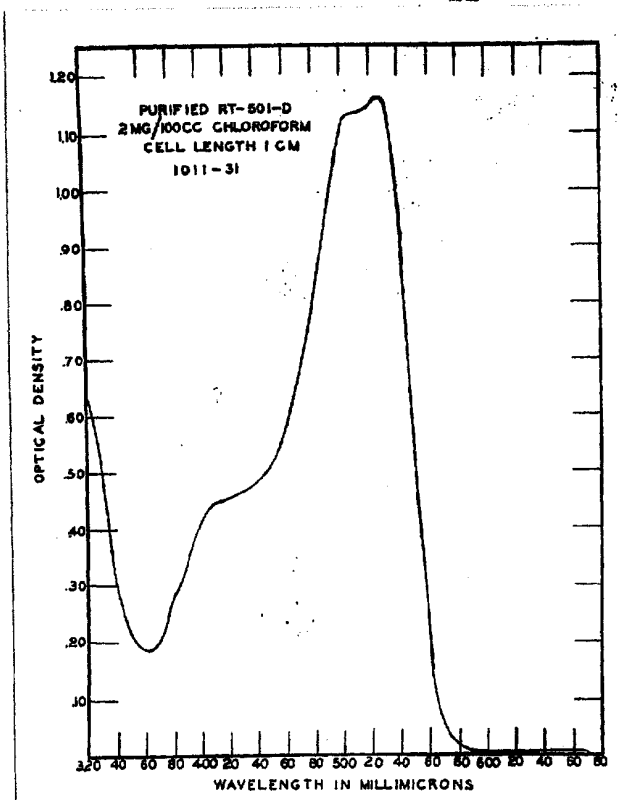


FIG. 3 - ABSORPTION SPECTRUM OF RT-501-D

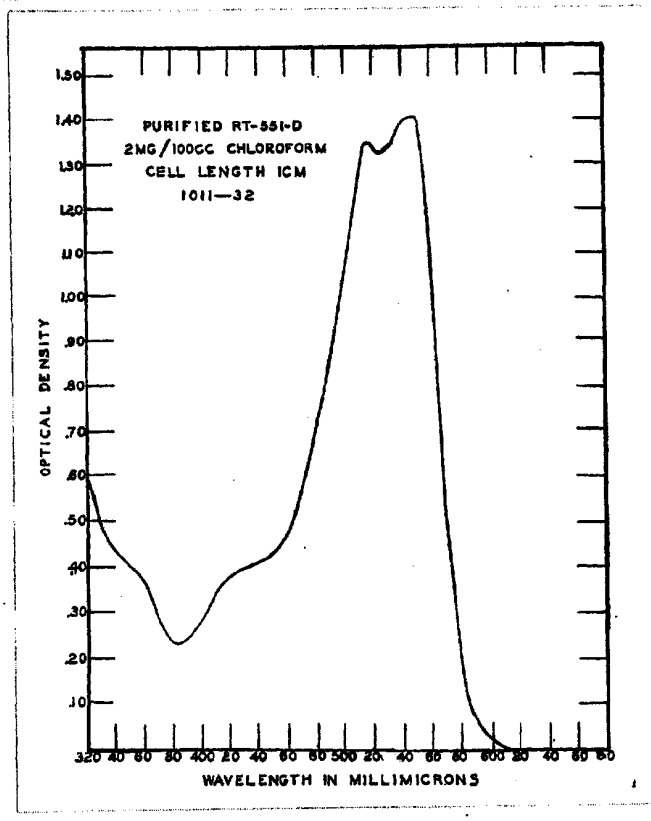


FIG. 4 - ABSORPTION SPECTRUM OF RT-551-D