1942

Dispersing agents for use with cadmium sulfide pigments.

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DISPERSING AGENTS FOR USE WITH CADMIUM SULFIDE PIGMENTS

A Thesis

Submitted to the Faculty

of the Graduate School

in Partial Fulfillment of the

Requirements for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

By

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May 15, 1942

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ACKNOWLEDGEMENT

This author wishes to acknowledge the kind assistance and helpful guidance of Dr. G. C. Williams who directed this research.

ABSTRACT

This thesis presents information on the effect of various dispersing agents on the dispersion of cadmium sulfide pigment in alkali refined linseed oil and an oleo-resinous varnish.

The dispersing agents investigated were nitrobenzene, oleic acid, Zinol, Glaurin, Nopco-1072, Nopco CVT, Vel, Lecivit "F",Nuade, Zinc Nuowetter,and Nuodex Zinc (8%).

The efficiency of the dispersion resulting from the addition of each was evaluated by three methods. First by the percent pigment that could be added to produce a ground paste of standard consistency, and the percent pigment that could be added to produce a paint of standard consistency. Next dispersion was evaluated by noting the volume of pigment that settled in a unit time, due both to gravity and centrifugal force. Lastly the degree of dispersion was observed under a microscope.

Although no general satisfactory dispersing agent was found in this investigation, several existing methods of evaluating dispersion were utilized and one new method was developed.

I N T R O D U C T I O N

The degree to which a pigment is dispersed in a paint or enamel greatly affects the properties of the paint or enamel and the subsequent films. The effect is evident in the consistency and settling properties of the paint, as well as in the drying, gloss, and weathering characteristics of the film.

It has been demonstrated by extensive experimentation that the optimum dispersion varies from the ultimate degree down to that of a relatively large flocculation. Through the use of equipment that has been available for sometime low to medium dispersions could be easily produced, but the production of fine dispersions has been a generally unsolved problem. The greatest advances in this direction have been the design of superior grinding equipment and the formulation of vehicles to give a satisfactory dispersion. However, even with these advancements, many pigment-vehicle combinations remain as "hard grinders", difficult to disperse with any reasonable amount of grinding. As a result chemicals called dispersing aids have been added to the paint formulation to decrease the tendency toward flocculation and the grinding time.

Cadmium colors are non-bleeding, light-fast pigments that bake well, but have the undesirable property of being very hard to disperse in the usual paint and varnish vehicles. As a result, cadmium paints result in films that chalk quickly and badly. The purpose of this investigation is to study the problem of dispersing cadmium sulfide pigments in alkali refined linseed oil and in an oleo resinous varnish.

H I S T O R I C A L

Paint making, believed to have originated in Egypt, is one of the oldest sciences on record. Accounts of excavations state that as far back as 4000 B.C. traces of color were found preserved in the form of writing and pictures painted on walls of tombs.

Additional agents in paints were found through a need to overcome existing deficiencies. Probably the first substances of this nature were driers, such as metallic salts added to perform the special duty of hastening drying of the paint film. As numerous pigment-vehicle combinations were developed, further addition agents were produced to alleviate specific undesirable characteristics. These agents, for example, affected shelf settling, livering, skinning, etc.

For the past decade the use of agents to increase dispersion and decrease grinding time has been of interest to paint manufacturers. Articles have been published during this time discussing effective dispersing agents in specific pigment-vehicle combinations and some methods for evaluating the efficiency of dispersion due to these agents.

Probably more agents have been investigated to aid in the dispersion of carbon black than any other pigment, and include such proprietary compounds as zinc naphthenate, zinc dichlorstearate, "Nuowetter 2 number 1000", and naphthenated castor oil. (19,18,11)

In 1935 the New York Production Club tested thirteen dispersing agents representing eleven classes of compounds. These were tested on a series of white and colored pigments in linseed oil and varnish vehicles. The compounds were found to be effective on specific pigments and are listed in order of numerical superiority; zinc naphthenate, Lecivit, Twitchel Base 265, ester gum, oleic acid, Emulsiphor "A", salicylic acid, and nitrobenzene.(16) The Detroit Production Club (19,3) made an extensive study of dispersion aids, testing over fifty agents in various pigment-vehicle combinations. After two years of observation and study of these agents it was found the following aided dispersion of decreased grinding time in at least several cases: Nuade, Zinol, Glaurin, Lead Oilsolate, Zinc Aerosol-OT, Nopco-2180, Tergitol No.4, Nopco-CVU, Nopco-CVT,Tergitol No. 7, Talloil No. 1, diethylene glycol dinaphthenate, Sharples Agent No. 2, and Nopco-CMH.

A number of methods have been devised for evaluating the effects of dispersing agents on mixed paints. In general all these methods are relative, and the evaluation is made on the comparative effectiveness of different agents.

Selden and Selker (18) proposed that if a number of paint samples were ground to a standard fineness, the degree of dispersion would be directly proportional to the grinding time. They ground a number of paste samples on a pebble mill with different agents added to each. They considered their grind to be of standard fineness when it gave a specified reading on a Sherwin-Williams fineness gauge. The time required for the grind was chosen as an indication of effectiveness.

The New York Production Club (15) in 1934-35 evaluated dispersion in much the same manner. They mixed, ground, and tested samples with different dispersing agents added under constant conditions. The degree of dispersion was judged by fineness readings obtained on standard glass plates, and evaluated as finer, equal to, slightly coarser, or coarser than a sample with no agent added. The relative effect of these agents on the brushing, leveling, sagging, fading, and drying properties of the film, and the consistency of the paint was noted.

In the work of dispersing agents undertaken by the Detroit Production Club (5), several methods of evaluating dispersion were used. The major portion of the work was done on a small laboratory roller mill. The mill was properly adjusted, and the time required for a paste with no agent added to pass once through the mill was noted by means of a stop-watch. Next pastes with incorporated addition agents were passed through the mill without changing the mill setting. The differences between these grinding times and the grinding time for the blank were used to give a relatine evaluation of dispersion. The Club also used sedimentation volumes to evaluate efficiency by dispersion. Tests were made by placing twn grams of pigment paste in a test tube, and adding ten grams of toluene. The mixture was then shaken and left to stand for twenty-four hours. At the end of this period measurements were made of the volumes of pigment that had settled to the bottom of the test tube. The agents giving less sediment were judged to be the best dispersion aids.

The Detroit Club is also responsible for studies of dispersion by means of X-ray diffraction patterns, and by making photomicrographs of paste smears on a microscopic slide. (5)

The phenomenon of dispersion has also been observed by determining the tintorial strength of the pigment-vehicle combination. It was shown that if the added agent is effective as dispersion agent, the tintorial strength of the paste containing it is greater than a similarly ground pure paste. (11)

The following outstanding generalizations have been made from the previous work on this subject:

(1) The optimum amount of dispersing agent is from one to one and one-half percent, based on the weight of pigment used. Also it is immaterial whether the agent is added to the grinding liquid, or whether the pigment partucles are coated. (15)

(2) Dispersing agents are very specialized, that is, an agent may be effective for one pigment-vehicle combination while it has no tendency to aid dispersion with different pigments and in different vehicles.(5)

(3) With an effective dispersing more pigment can be added to a paste before producing a standard consistency. (5)

(4) Grinding time is generally, but not necessarily, decreased because of better dispersion while it is always decreased, up to the loading limit, by an increase in pigment concentration. (5)

T H E O R E T I C A L

The terms wetting and dispersing are often used synonymously in the paint industry although they are entirely different and distinct phenomena. This use may lead to the confusion unless there is a clear differentiation between the two terms.

The wetting of a paint pigment by a vehicle is the displacing of air on the surface of the pigment particle by the vehicle. It is strictly a surface phenomenon, based not only on the reduction of surface tension of a solution but also upon the reduction of interfacial tension between the solid and the liquid.

Dispersion is the breaking up of the clusters of pigment particles, and suspending the individual particles in the vehicle. Then the pigment is immersed in the grinding liquid, absorption occurs, forming a layer of oriented molecules around each pigment particle. The energy change, E, that occurs during this absorption process is given by the formula $E - S_{12} - S_{10} - S_{02}$. S_{12} is the interfacial energy between pigment and vehicle before absorption takes place, S_{10} the interfacial energy between pigment and absorbed layer, and S_{02} the interfacial energy between absorbed layer and vehicle. As dispersion depends largely upon the properties of the oil and to only a small extent upon the surface properties of the pigment, S_{02} is the predominant factor. (14)

In dispersion, the continuous phase of oriented molecules is broken, and two areas of interfacial surface S_{02} are created. The energy change, work of dispersion, may therefore be formulated $E_d - 2S_{02}$. The flocculation process is just the reverse of the dispersion process and may be formulated $E_f - 2S_{02}$.(14)

This indicates that when the interfacial energy, S_{02}, between the adsorbed layer and the oil is high, the work of flocculation is large and positive; that a large amount of energy is expended by the system when flocculation occurs; and that the flocculated state is much more stable than the dispersed state. A high value of S_{02} will therefore tend to bring about flocculation. On the other hand, when the interfacial energy S_{02} is small, the work of flocculation will likewise be small, and the system will tend to be more stable and will remain dispersed longer. (14)

An effective agent is usually a polar material having a portion which has an attraction for the vehicle and a portion which has an attraction for the pigment.

As the dispersing agent orients on the pigment surface, there should be a metastable bond between the pigment and agent, while the polar complex, being attracted by the vehicle, should orient itself to present a new or pseudo surface that is similar to the vehicle. This will keep the pigment particles from grouping together and permit them to move about in the paint liquid. An example of a pigment, agent, vehicle system is zinc oleate used as a dispersing agent. The pigment particles are likely to attract the zinc portion, while the polar oleate radicle is orientated towards the vehicle.(10,3)

Proper grinding is necessary for proper dispersion. In the process of mixing, a sufficient quantity of vehicle is mixed with the clusters of pigment particles to wet them. Next the clusters are placed on a mill so that they will be torn apart by the shearing action developed which exposes new surfaces for further wetting. Grinding seldom reduces the size of the pigment particles, primarily it breaks up the aggregates. The average pigment particle ranges in size from less than 1 to 10-15 microns. As the minimum clearance that can be obtained on a roller mill is 15-25 microns, it can be seen that grinding may be obtained from the rolls alone, but from a high viscosity paste coating the mill. A roller mill that is initially set too close will cause the oversize, or large agglomerates, to hold back and not pass through until last. When they do pass, they push the rolls apart, which results in an uneven grind. The correct procedure is to set the rolls to grind the oversize, then to reduce the clearance until all the fines have been ground. (1)

One phase of the experimental work in this thesis is set up on the phyothesis that the consistency of a paste or paint decreases with better dispersion. When a paint is flocculated a number of pigment particles are held together, forming loosely grouped masses which act as a unit. Part of the vehicle is trapped within these units and creates the effect of a much higher pigment concentration. When these flocs are broken up and the individual pigment particles dispersed, they can move freely in the liquid mass resulting in a much lower consistency paste. This may be better pictures by comparing the pigment particles and flocculates to the molecules of a liquid. Just as lower molecular weight liquids, smaller molecules, have low viscosities because of less resistance to movement, so does better dispersed paints have lower consistency. (12) Therefore, if constant pigment-vehicle ratio paint samples are made up with a small amount of dispersing agent in each, the samples should vary in consistency relative to the degree of dispersion. The more effective the dispersion aids, the lower will be the consistency of the samples and the higher will be the percent pigment that can be added to a standard consistency paste. This will hold true for both paste and paint if all the samples are mixed, ground, and tested for consistency in exactly the same manner.

It frequently happens that a paint having a quite heavy structural body before it is stirred will become thinner and more free-flowing upon agitation. A paint showing these tendencies is termed thixotropic. (7) It was endeavored to keep away from thixotropic paints in this investigation.

The nature and degree of dispersion has an effect on the pigment suspension of the paint. It is quite generally known that a well dispersed pigment will settle slowly but to a hard cake, while a flocculated pigment will settle tapidly to a soft cake. This is because of the fact that when the pigment is dispersed by some agent the original specific gravity of the pigment is generally replaced by an apparent specific gravity that is much less, which markedly affects the rate and type of settling. Thus if samples containing different dispersion aids, but constant pigment-vehicle ratios, are allowed to settle for a definite time, the ratio of pigment settled to paint initial will be low for effective dispersing aids and high for ineffective dispersing aids. The settling may be forced, as when centrifuged or natural. However, with effective agents the pigment will settle to a hard cake while with ineffective agents the settled cake will be soft.

Another method of evaluating dispersion is by examination under a microscope at from 400 to 500 magnifications. When a pigment dispersion is viewed under a microscope the pigment particles appear individually, with each particle having a separate movement. When a flocculation is viewed, the pigment particles appear in clisters, the size and number of the clusters depending upon the degree of flocculation.

The type of substance used as a dispersing aid should be a polar material preferably of high molecular weight. Materials of low molecular weight are more readily adsorbed on the pigment surface, but are not as efficient in dispersion. The chain must not be too long, because the agent would form a solid or semi-solid complex yielding a rigid paste.

A review was made of the dispersing agents used by the trade and reported in literature. A selection of the specific agents to be tested was taken from this review, and were chosen because they were common, economical, easily obtainable, and represented a large variety of chemical types.

The dispersing agents to be investigated are nitrobenzene, oleic acid, Zinol, Glaurin, Nopco-CVT, Vel, Lecivit "F", Nuade, Zinc Nuowetter, Nopco-1072, and Nuodex Zinc (8%).

E X P E R I M E N T A L

RAW MATERIALS

The raw materials used in this investigation were cadmium yellow pigment, alkali refined linseed oil, Durez ester gum varnish vehicles, and eleven dispersing agents. The dispersing agents used were nitrobenzene, oleic acid, Zinol, Glaurin, Nopco-CVT, Vel, Lecivit "F", Nuade, Zinc Nuowetter, Nopco-1072, and Nuodex Zinc (8%).

The properties of the raw materials are listed as follows:

Cadmium Yellow-1475 -- This cadmium sulfide pigment was manufactured by the Kentucky Color and Chemical Co. It sells at present for $1.75 per pound. It is a medium yellow, permanently non-bleeding, light-fast, and alkali-resisting pigment. Cadmium yellow of this type has a specific gravity of 4.25 and a bulking value of 35.40 pounds per gallon. The residue on a 325 mesh screen was 0.02 percent, and its oil absorption was 17.42. (8)

Alkali Refined Linseed Oil -- This oil was alkali refined by Peaslee-Gaulbert Paint and Varnish Co. It is pale yellow in color. Linseed oil of this type has a specific gravity of 0.931 to 0.935, an index of refraction of 1.478, an iodine number of 175 to 190, and a saponification value of 188 to 196. (8)

Durez Ester Gum Varnish-No.550 -- This was a special varnish in that it had no drier added. The constituents of the varnish were 25 pounds Durez phenolic resin, 75 pounds ester gum, $3\frac{1}{4}$ gallons high bodied linseed, 20 gallons China wood oil, and 40 gallons of mineral spirits, for a 71 gallon yield. This varnish is of light yellow color, and it incorporates the property of high gloss, non-yellowing, and soap and water resistance to the paint film.

The properties of the dispersing agents are listed as follows:

Nopco-CVT -- This dispersing agent, an oleic amine, is manufactured by National Oil Products Co. It is a brown paste that melts at 37-39°C, is soluble in alcohol and oil, and insoluble in water. It has a specific gravity of 0.999.

Nopco-1072 -- This dispersing agent is also manufactured by National Oil Products Co. It is a liquid of medium brown color and high viscosity. Its melting point is 18-20°C. It is soluble in alcohol and oil, and insoluble in water. It has a specific gravity of 0.87.

Glaurin -- Manufactured by Glycol Products Co., is diethylene glycol mono-laurate. It is a light yellow, oily liquid that is slightly soluble in oil and completely insoluble in water. Its specific gravity is 0.96.

Zinc Nuowetter -- This dispersing agent is manufactured by Nuodex Products Company. It is a straw-colored, medium-viscosity liquid. It has a specific gravity of 1.026.

Nuade -- Manufactured by Nuodex Products Co., is a resinous type polymer. It is a neutral, non-reactive, dark brown, high viscosity liquid that bulks 7½ pounds to the gallon.

Nuodex Zinc (8%) -- This agent is also manufactured by Nuodex Products Co. It is a low-viscosity, light yellow, oily liquid. No physical data could be found on this agent.

Lecivit "F" -- An organic phosphatide, is manufactured by Jungman and Company. It is a liquid of very high viscosity and dark brown color. No physical data could be obtained on this agent.

Zinol -- Manufactured by Nuport Industries, is a zinc resinate. It is a low-viscosity, light yellow, oily liquid. No physical data could be obtained on this agent.

Vel -- A sulfonated alcohol, is manufactured by Colgate-Palmolive-Peet Co. It is a neutral hydrophylic detergent in the form of soap flakes.

Nitrobenzene -- A widely used organic chemical. It is a light yellow liquid, insoluble in water and soluble in alcohol and ether. Nitrobenzene has a molecular weight of 122.1, a boiling point of 210.9°C, and a specific gravity of 1.205.

Oleic Acid -- A well known organic chemical with a molecular weight of 282.5. It is a colorless liquid, insoluble in water and soluble in alcohol and ether, has a boiling point of 285°C and a specific gravity of 0.85.

PROCEDURE

The experimental work in this investigation was divided into two phases. The dispersing agents were first tested with cadmium yellow pigment in linseed oil, and secondly tested with cadmium yellow pigment in a varnish vehicle.

LINSEED OIL VEHICLE

The efficiency of the dispersion resulting from the addition of each agent to linseed oil vehicle was evaluated by three methods. First by the percent pigment that could be added to produce a ground paste of standard consistency, and the percent pigment that could be added to produce a paint of standard consistency. Next dispersion was evaluated by noting the volume of pigment that settled in a unit time, due both to gravity and centrifugal force. Lastly the degree of dispersion was observed under a microscope.

The equipment used in obtaining the percent pigment that could be added to produce a standard consistency paste and a standard consistency paint, consisted of the following: a laboratory type, three-roll roller mill, a laboratory type triple beam balance, two glass plates and kilogram weight, stop clock,

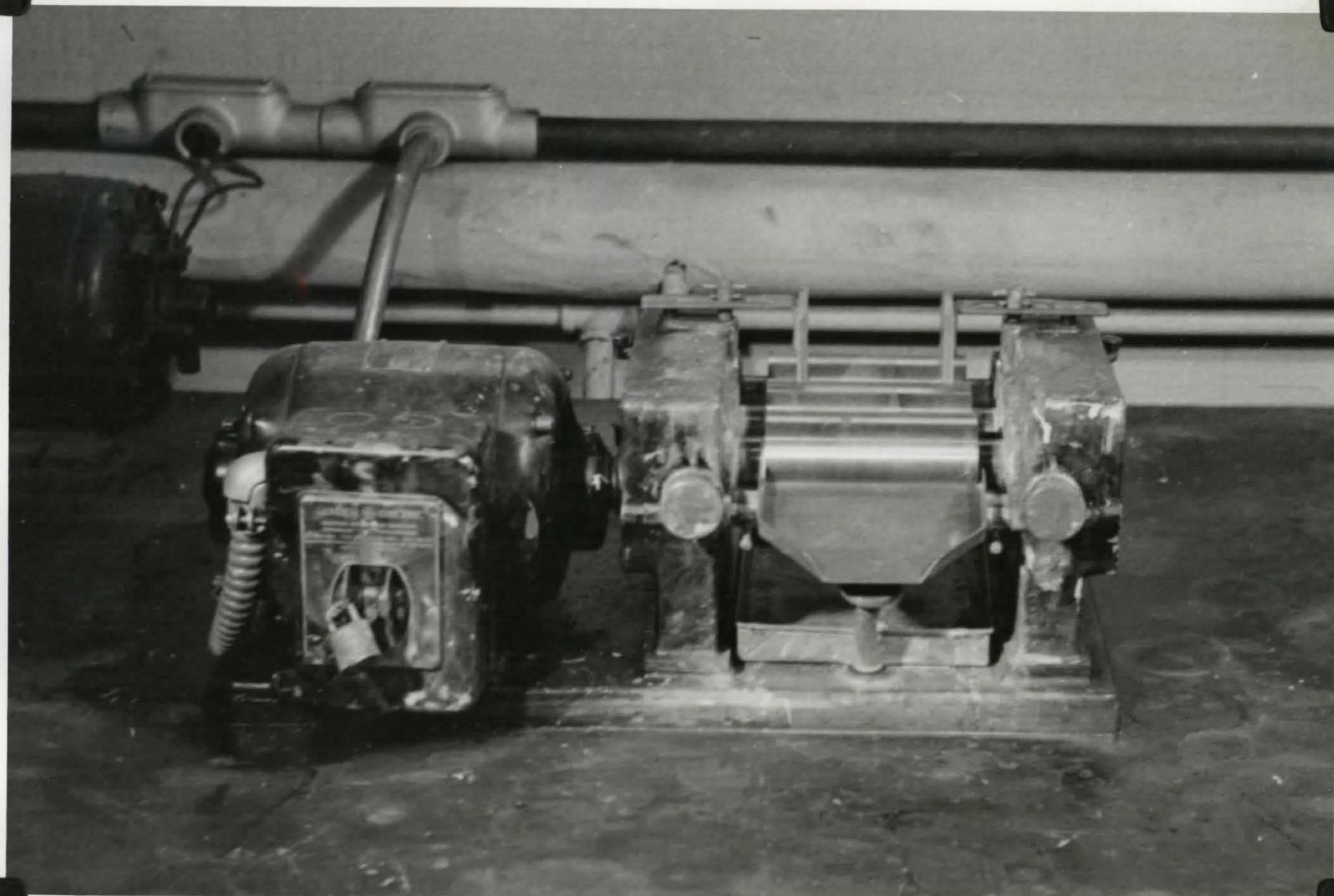

Figure 1

Roller-Type Paint Mill

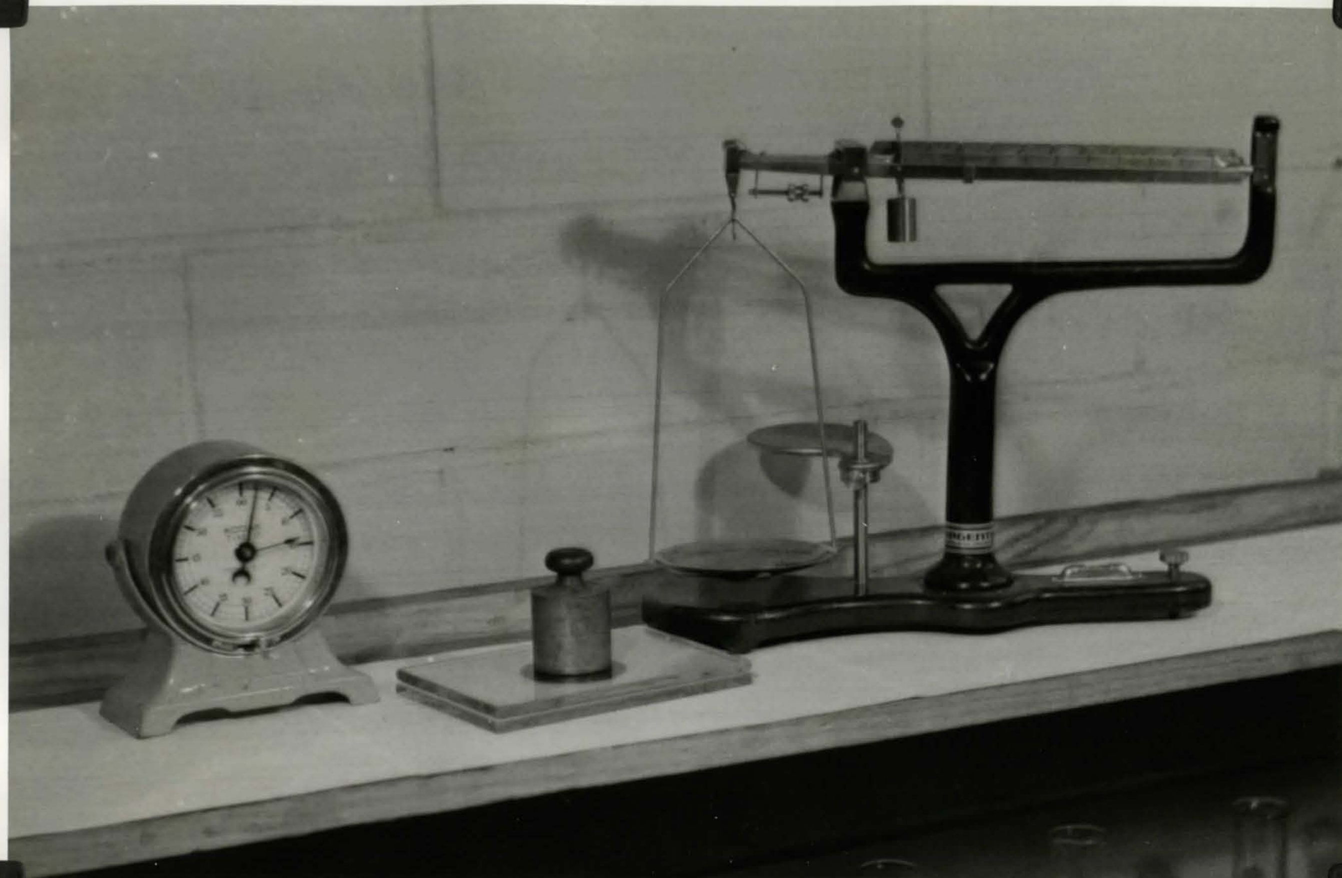

Figure 2

Apparatus for Testing Paste Consistency

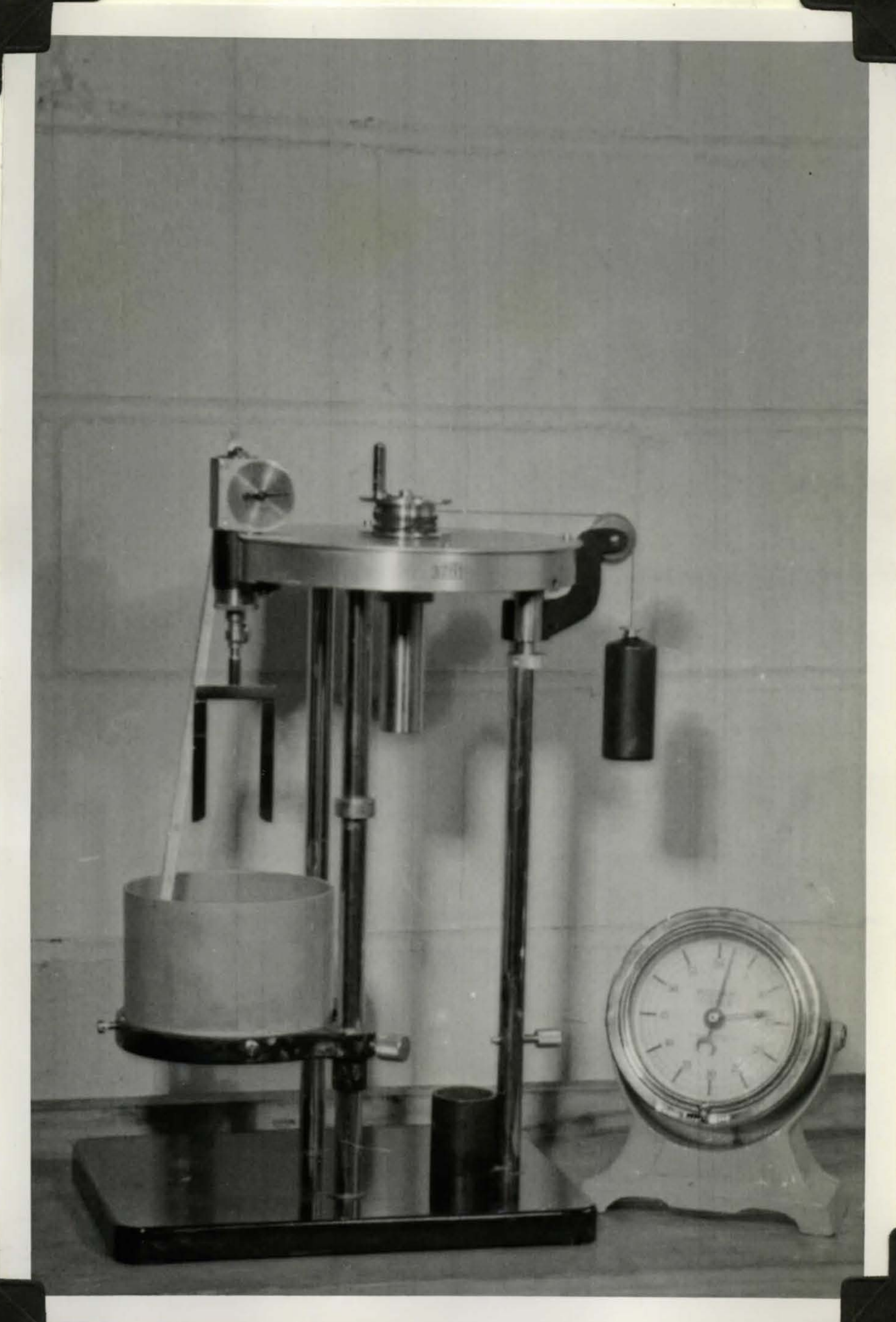

Figure 3

Stormer Viscometer

Stormer viscometer, and beakers and spatula for mixing the paste. The roller mill is shown in Figure 1, the glass plates, kilogram weight, and balance in Figure 2, and the Stormer viscometer in Figure 3.

The Stormer viscometer gave a very convenient and standard method for measuring paint consistency, but could be used to measure consistencies as high as that of paste. After a review of the existing methods of measuring paste consistencies a new method was devised. This method consists of pressing a known weight of paste between two glass plates for a definite time, and noting the diameter of the circle to which the paste spreads. When the pressure applied to the plates, the time of application, and the weight of paste between the plates are constant, the diameter of the circle to which the paste spreads will give a relative measure of the consistency. Experimentation determined that best results were obtained when a weight of one kilogram was applied for thirty seconds to one gram of paste.

The validity of this method was proved by mixing and grinding separate, constant, pigment-vehicle pastes in the same manner. When the consistency of these pastes was measured, the diameter of the circle to which the paste spread gave good checks. The materials used in

TABLE I TESTS FOR CONSISTENCY CONTROL, A

Run	Paste: Wt. Pig. (grams)	Paste: Wt. Oil (grams)	Testing: Wt. Paste Used (grams)	Testing: Wt. Applied (grams)	Testing: Time Applied (sec.)	Testing: Diam. of Circle (inches)
1-a	40.0	6.41	1.00	1000	30	0-29/32
1-b	40.0	6.41	1.00	1000	30	0-28/32
2-a	40.0	6.61	1.00	1000	30	1- 0/32
2-b	40.0	6.61	1.00	1000	30	1- 0/32
3-a	35.0	11.60	1.00	1000	30	2-14/32
3-b	35.0	11.60	1.00	1000	30	2- 9/32

Note: The figures for circle diameters were obtained by an average of three readings, taken 120 degrees apart.

this test were chrome yellow pigment and raw linseed oil vehicle. The results of this test are shown in Table I.

Further validity of the procedure was shown by the following method. A pigment oil paste of definite pigment concentration was mixed and ground on a roller mill. The consistency of this paste was measured by the method mentioned above. Next, using the same pigment and oil, an unknown pigment concentration paste was mixed and ground in similar manner. Oil was slowly added to this paste until the consistency reading was duplicated. The percent pigment in this paste checked with the original. The results of this test are shown in Table II.

Having proved the validity of the method for measuring the consistency of paste, the effect of the agents on the consistency of both the paste and the paint was tested. All tests were made by mixing samples to the same paste and paint consistencies, and noting the variations in the percent pigment added to the paste and paint by the dispersing agents. The procedure for testing the blank, no dispersing agent added, and samples with various agents added, was based on mixing, grinding, and testing in the same manner. The procedure for testing the blank and samples is as follows.

TABLE II TESTS FOR CONSISTENCY CONTROL, B

Run	Pigment	Wt. Pig. (grams)	Wt. Oil (grams)	Diam. of Circle (inches)	% Pig. In Paste
1-a	Chrome Yellow	35.0	9.28	2- 2/32	79.2
1-b	Chrome Yellow	35.0	9.12	2- 2/32	79.3
2-a	Zinc Oxide	30.0	7.43	2- 5/32	80.2
2-b	Zinc Oxide	31.8	8.11	2- 6/32	79.7
3-a	Zinc Oxide	30.0	5.91	1-30/32	83.7
3-b	Zinc Oxide	35.0	6.84	1-30/32	83.7
3-c	Zinc Oxide	30.0	5.96	1-31/32	83.5

Note: All tests were made with acid refined linseed oil vehicle. The figures for circle diameter were obtained by an average of three readings, taken 120 degrees apart.

Blank -- Oil was added to a weight amount of pigment until a heavy paste was obtained. The method of mixing and the weight of oil was recorded. This paste was then ground on a three-roll roller mill until the consistency did not change with succeeding passes. The number of passes was recorded and the setting of the mill observed. The consistency of the paste was measured after each two passes by the method previously described. The percent pigment in a paste of the final consistency was recorded.

A weighed portion of this paste was then placed in a container adapted to the Stormer viscometer, thinned with oil to a paint consistency, and the weight of added oil recorded. The consistency of this paint was measured on the viscometer, and the percent pigment in the paint calculated.

Sample: -- For each sample, 1.5 percent of agent, based on weight of pigment used, was incorporated in a small amount of oil. This oil was added to the same weight of pigment as used in blank. Additional oil was added until a paste of grinding consistency was obtained. This paste was ground on the roller mill at the same setting as for the blank. Readings of paste consistency were taken after each pass and oil added to the paste on the mill if necessary. When the paste had a consistency equal to that of blank, after at least the same number of passes, the percent pigment in the paste was calculated.

A weighed portion of this paste was thinned with oil until it had a consistency equal to the blank. The Stormer viscometer was used to determine this consistency. The weight of oil added was recorded and the percent of pigment in the paint calculated. Several duplicate runs were made on each sample to verify the results.

The following is an example of how the date was obtained for the blank and one of the samples.

Blank:

Weight of Pigment = 65.00g.

Wt.volumetric flask + oil = 99.18g. (initial)
" " " + " = 82.85g. (final)
Total wt.oil to make paste = 16,33g.

Paste Consistency Readings:

Diam. = 3.7cm. (mixed + two passes on mill)
= 4.0cm. (3rd pass on mill + oil added)
= 4.2cm. (5th " " " + " ")
= 4.2cm. (6th " " ")

Percent pigment in paste = $\frac{65.0}{65.0 + 16.33}$ x 100 = 80.0%

Wt.can + paste = 102.01g.
Wt.can = 28.41g.
Wt.paste = 73.60g. ' 58.7g. pigment
' 14.9g. oil

Wt.volumetric flask + oil = 82.82g. (initial)
" " " + " = 58.70g. (final)
" oil added to paste = 24.15g.

Paint Consistency (read on viscometer):

Time = 36.0 sec.
= 33.5 " (oil added)
= 31.5 " (" ")
= 31.0 " (" ")

Percent pigment in paint = $\frac{58.7\text{x } 100}{58.7+24.12+14.9}$ = 60.1%

Note: 150 gram weight was used on viscometer.

Sample: Dispersing agent -- Zinol

Weight Pigment = 70.00g.
1.05g. Zinol added to 7.0g. oil

Wt. volumetric flask + oil	= 27.41g.
" " " + agent	= 19.97g.
" oil - agent added	= 7.44g.

Wt. volumetric flask + oil	= 63.47g. (initial)
" " " + "	= 58.71g. (final)
" oil added	= 4.76g.

Paste Consistency Reading:

Diam. = 3.8cm. (before grinding)
= 3.5cm. (after 2 passes)
= 3.7cm. (" 4 " + oil)
= 4.2cm. (" 6 " + oil)

Percent pigment in paste = $\frac{70.0 \times 100}{70.0 + 12.2}$ = 85.2%

Wt. can + paste	= 104.55g.
" "	= 28.43g.
" paste	= 76.12g. ' 64.9g. pigment ' 11.2g. oil

Paint Consistency (read on viscometer):

Time = 35.0 sec.
= 32.5 " (oil added)
= 31.0 " (" ")

Percent pigment in paint = $\frac{64.9 \times 100}{64.9 + 28.55 + 11.2}$ = <u>62.0%</u>

The results of all the runs, made in a similar manner, are shown in Table III.

TABLE III PIGMENT CONCENTRATION IN PASTE AND PAINT

Run	Agent	% Pig. in Paste	% Pig. in Paint
1	Blank	----	63.7
2	"	86.7	64.7
3	"	86.5	65.0
4	"	86.8	64.7
5	"	86.3	----
		86.6 Average	64.2 Average
6	Lecivit "F"	85.1	62.8
7	"	84.7	----
8	"	85.2	62.1
		85.0 Av.	62.4 Av.
9	Nitrobenzene	----	63.0
10	"	85.5	63.3
11	"	85.6	63.4
12	"	85.0	----
		85.4 Av.	63.2 Av.
13	Zinol	85.2	62.0
14	"	85.0	62.2
		85.1 Av.	62.1 Av.
15	Oleic Acid	84.2	60.8
16	" "	83.6	60.3
		83.9 Av.	60.5 Av.
17	Glaurin	81.5	60.2
18	"	82.8	61.4
		82.1 Av.	60.8 Av.
19	Zinc Nuowetter	86.3	62.6
20	" "	86.4	63.2
		86.35 Av.	62.9 Av.
21	Nopco-CVT	82.3	56.0
22	"	82.8	----
23		----	56.3
		82.5 Av.	56.2 Av.

TABLE III - Continued.

Run	Agent	% Pig.in Paste	% Pig.in Paint
24	Nuade	86.3	63.3
25	"	86.2	63.2
		86.25 Average	63.25 Average
26	Nopco-1072	88.4	65.2
27	"	88.5	65.2
		88.45 Av.	65.2 Av.
28	Vel	85.1	62.3
29	"	85.3	62.3
		85.2 Av.	62.3 Av.
30	Nuodex Zn(8%)	85.3	62.8
31	"	86.5	63.5
32	"	86.2	63.8
		86.0 Av.	63.4 Av.

The equipment used in testing by sedimentation methods the effects of the various agents on dispersion consisted of test tubes, and a high speed centrifuge. The centrifuge is shown in Figure 4.

Sedimentation tests were made by gravitational and centrifugal methods. The above samples, after the consistency of the paint was determined, were placed in test tubes and left to stand. After three months, a volume ratio of pigment settled to initial paint present was recorded. The readings were obtained by measuring, in constant volume tubes, the height of pigment settled and height of initial paint. Also the type of cake to which the pigment settled was noted. The results are shown in Table IV.

Each sample was again well mixed to return to a uniform distribution of pigment and oil. This time they were centrifuged at the same speed for periods often and forty minutes. At the end of each period the ration of pigment settled to paint initial was recorded. At the end of the forty minute period, the type of cake to which the pigment had settled was noted. These data are shown in Table V.

Figure 4

High Speed Centrifuge

TABLE IV -- NORMAL SETTLING

Agent	Ratio pigment Settled to Total	Type of Cake
Zinol	0.474	Very hard
Nitrobenzene	0.500	Average hard
Nitrobenzene	0.492	"
Lecivit "F"	0.528	"
Lecivit "F"	0.535	"
Blank	0.471	"
Blank	0.483	"
Glaurin	0.578	"
Zinc Nuowetter	0.508	"
Zinc Nuowetter	0.508	"
Nopco-CVT	0.579	Medium hard
Nopco-CVT	0.568	"
Nuade	-----	None, color deeper toward bottom
Nuade	-----	"
Nopco-1072	0.324	Soft
Vel	0.584	Medium hard
Nuodex Zinc (8%)	0.565	"
Oleic Acid	0.567	Average hard

TABLE V -- CENTRIFUGE EFFECTS IN OIL

Agent	10 minutes Ratio	40 minutes Ratio	Appearance of Liquid after 40 minutes
Zinc Nuowetter	3.8/4.7-.808	2.2/4.7-.457	Slightly cloudy
Zinc Nuowetter	3.4/4.4-.781	1.9/4.4-.434	" "
Lecivit "F"	2.4/4.5-.534	2.0/4.5-.444	Clear
Lecivit "F"	2.6/4.8-.537	2.1/4.8-.432	"
Vel	3.6/4.5-.578	2.1/4.5-.442	"
Nopco-1072	3.8/4.5-.844	2.0/4.5-.444	Cloudy
Nuade	Very slight cake,color deeper toward bottom		
Nuade	Very slight cake,color deeper toward bottom		
Nopco-CVT	2.6/4.7-.536	2.1/4.7-.447	Clear
Nopco-CVT	2.1/4.7-.437	1.9/4.7-.404	"
Nuodex Zinc(8%)	3.8/4.7-.807	2.2/4.5-.478	Slightly cloudy
Nitrobenzene	4.2/5.1-.833	2.6/5.1-.515	Clear
Nitrobenzene	3.9/4.5-.877	2.3/4.5-.506	"
Blank	4.3/4.9-.887	2.9/4.9-.598	Cloudy
Blank	4.4/5.0-.881	3.0/5.0-.600	"
Glaurin	3.4/4.8-.716	2.3/4.8-.485	Clear
Zinol	4.1/4.7-.871	2.3/4.7-.495	"
Oleic Acid	2.5/4.6-.533	2.0/4.6-.435	"

Note: All centrifuging was done at same speed. After centrifuging Nuade samples for a total of 3½ hours there was no apparent change. Ratio is centimeters of pigment suspended to centimeters of paint initial.

Having returned the samples to a uniform pigment distribution of the relative dispersions of each was observed by use of a microscope at 425 magnifications. The specimens were thinned on the slide with the grinding vehicle for this observation. The samples were then centrifuged for periods of seven, ten, fifteen, and twenty minutes and the degree of dispersion observed with microscope at the end of each period. The purpose of centrifuging was to see to what degree, and at what rate, the flocculates would be thrown out. The degree of dispersion was evaluated from one to four, one a good dispersion, four a bad flocculation, and two and three intermediates. These data are shown in Table VI.

TABLE VI -- MICROSCOPIC COMPARISONS IN OIL

Agent	Shaken Well	Cent. 7 min.	Cent. 10 min.	Cent. 15 min.	Cent. 20 min.
Blank	4	2	2	1½	1½
Blank	4	2	2	1½	1½
Zinc Nuowetter	4	3	2½	1½	1½
Zinc Nuowetter	4	2½	2	1½	1½
Nuade	3½	2½	1½	1+	1+
Nuade	3½	2½	1½	1+	1+
Nitrobenzene	4	3	2½	2	1½
Nuodex Zinc(8%)	3½	2	1½	1+	1+
Zinol	4	3	3	2	1½
Vel	4	3	2½	2	1½
Lecivit "F"	4	3½	2½	2	1½
Glaurin	4	3½	2½	2½	1½
Nopco-CVT	4	3	3	2½	1½
Nopco-1072	3½	2	1½	1+	1+
Oleic Acid	4	3½	2½	2	1½
Nitrobenzene	4	3½	2½	2	1½

Note: One is good dispersion, four is bad flocculations, and two and three are intermediates.

VARNISH VEHICLE

When ester gum varnish was used as vehicle, the grinding procedure had to be changed to some degree. It was found that when grinds were made on the roller mill, evaporation of the volatile constituents in the varnish was so rapid that paste consistency readings could not be duplicated. To overcome this, the samples and blank were ground in jars on a ball mill. As before, the efficiency of dispersion was evaluated by the percent pigment that could be added to a standard consistency enamel, by sedimentation tests, and by examination of the dispersion under a microscope.

To prove the validity of this new method of grinding, samples of exact pigment-varnish ratios were ground on the ball mill. Conditions such as grinding time, size of jars for grinding, and weight of balls were kept constant. The same weight of each ground sample was then reduced with varnish to a constant pigment-varnish ratio, and readings of consistency compared on the Stormer viscometer. A very good check of consistency readings were obtained as shown in Table VII.

TABLE VII TEST OF CONSISTENCY CONTROL IN VARNISH

Run	Wt. Pig. (grams)	Wt. Var. (grams)	Grind Time (Min.)	Wt. Var. Added (grams)	% Pig. in En.	Consistency
1-a	114.2	69.9	550	25.1	49.9	28.5
1-b	114.2	69.9	550	25.1	49.9	28.5
2-a	138.8	67.2	1000	6.9	63.6	41.25
2-b	138.8	67.2	1000	6.9	63.6	41.74

Note: The pigment used was cadmium yellow, and the vehicle ester gum varnish. The consistency reading is an average of several readings, taken on the Stormer viscometer.

The ball mill used consisted of three 2 inch cylindrical rolls spaced approximately 2½ inches apart. The center roll was driven by a ½ horsepower motor at a speed of approximately 85 revolutions per minute. The mill is large enough to accompany from ten to twelve jars at the same time.

In the procedure for evaluating the percent pigment that could be added to a standard consistency enamel, the paint was ground in twelve glass jars. To eleven jars were added 115.0 grams of cadmium pigment, 48.8 grams of ester gum varnish, 350.3 grams of case hardened steel balls, and 1.20 grams of a different dispersing agent. The remaining one was the blank to which was added 115.0 grams of pigment, 50.0 grams of varnish, 350.3 grams of balls, and no dispersing agent. All were ground for twelve hours and a half, sufficient time to obtain a good grind. A definite weight of the sample was then reduced with varnish to a standard consistency, measured on a Storm viscometer. The weight of varnish added was recorded and the percent pigment in enamel calculated. Check runs were run in this manner on all the dispersing agents and the blank.

The following is an example of how the data were obtained for the blank and several of the samples.

To all jars add:

115.0 grams cadmium yellow

50.0 grams ester gum varnish

350.3 grams steel balls

To: 1. No agent added

2. 1.20 grams Glaurin added

3. 1.20 grams Zinol added

All were ground on ball mill for 755 minutes plus three minutes to mix before reducing.

Testing:

1. Blank

Wt. can + enamel = 198.5g.
" " = 28.6g.
Wt. enamel = 69.9g. ' 53.9g. pigment
' 16.0g. varnish

Wt. vol.flask + varnish = 87.6g. (initial)
" " " + " = 50.2g. (final)
Wt. varnish added = 37.4g.

Testing Consistency of Enamel (on viscometer)

Time = 35.0 sec.
= 35.25 "

Percent pigment in enamel = $\frac{53.9 \times 100}{53.9+16.0+37.4} = \underline{50.2\%}$

Note: 150g. weight used on viscometer for all tests.

2. Glaurin

Wt. can + enamel = 127.9g.
" " = 28.7g.
" enamel = 99.2g. '69.1g. pigment
'30.1g. varnish

Wt. vol flask + varnish = 83.65g. (initial)
" " " + " = 45.30g. (final)
Wt. varnish added = 38.35g.

Testing Consistency of Enamel (on viscometer)

Time = 51.00 sec.
= 45.00 "
= 39.00 "
= 37.00 "
= 36.25 "
= 35.00 "

Percent pigment in enamel = $\frac{69.1 \times 100}{69.1+30.1+38.35}$ = 50.27

3. Zinol

Wt. can + enamel = 124.6g.
" " = 28.8g.
" enamel = 95.8g. ' 66.8g. pigment
' 29.0g. varnish

Wt. vol. flask + varnish = 85.04g. (initial)
" " " + " = 41.63g. (final)
" varnish added = 43.41g.

Testing Consistency of Enamel (on viscometer)

Time = 46 sec.
= 42 "
= 39 "
= 37 "
= 35 "

Percent pigment in enamel = $\frac{66.8 \times 100}{66.8+24+43.4}$ = 47.87

The results of these and similar tests are shown in Table VIII.

TABLE VIII - Pigment Concentration in Enamel

Run No.	Agent	Percent Pigment in Enamel
1	Blank	50.2
2	"	49.9
		50.1 Average
3	Glaurin	50.2
4	"	49.3
		49.8 Av.
5	Zinol	47.8
6	"	47.4
		47.6 Av.
7	Nuade	48.3
8	"	49.0
		48.7 Av.
9	Nuodex Zn (8%)	49.2
10	"	40.2
		49.2 Av.
11	Zn Nuowetter	48.8
12	"	49.5
		49.2 Av.
13	Lecivit "F"	49.7
14	"	50.1
		49.9 Av.
15	Nopco-1072	42.8
16	"	43.0
		42.9 Av.
17	Nopco-CVT	46.7
18	"	46.7
		46.7 Av.
19	Vel	49.2
20	"	49.6
		49.4 Av.
21	Oleic Acid	45.8
22	"	45.4
		45.6 Av
23	Nitrobenzene	57.3
24	"	54.0
		53.9 Av.

The procedure and equipment for evaluating the efficiency of dispersion by sedimentation tests, and by examination under a microscope in varnish vehicle is the same as when linseed oil vehicle was used. The data obtained by sedimentation tests and by examination under a microscope are listed in Table IX and Table X respectively.

TABLE IX - CENTRIFUGE EFFECTS IN VARNISH

Agent	10 minutes Ratio	40 minutes Ratio	Appearance Cake	Appearance Liquid
Zinc Nuowetter	1.5/4.5-.322	1.2/4.5-.267	Hard	Cloudy
Nuade	1.4/4.6-.294	1.3/4.6-.282	"	"
Zinol	1.6/5.3-.303	1.5/5.3-.276	"	"
Blank	1.5/4.9-.299	1.3/4.9-.268	"	"
Nuodex Zinc(8%)	1.6/5.2-.298	1.4/5.2-.269	"	"
Glaurin	1.4/4/9-.289	1.2/5.0-.240	"	"
Oleic Acid	1.4/4.4-.318	1.2/4.4-.273	Average	"
Nopco-1072	1.7/4.7-.362	1.3/4.7-.277	"	Clear
Nopco-CVT	1.8/4/7-.372	1.2/4.7-.266	Hard	Cloudy
Vel	1.8/5.0-.350	1.7/5.0-.330	"	"
Nitrobenzene	1.7/4.8-.355	1.5/4.8-.313	"	"
Lecivit "F"	2.0/5.4-.375	1.6/5.4-.297	"	"

Note: All centrifuging was done at same speed. Ratio is centimeters of pigment suspended to centimeters of paint total.

TABLE X - Microscopic Comparisons in Varnish

Agent	Shaken Well	Cent. 7 Min.	Cent. 10 Min.	Cent. 15 Min.	Cent. 20 Min.
Zinc Nuowetter	4	2½	1½	1½	1+
Nuade	4	2	2	1½	1½
Nitrobenzene	3½	2	1½	1+	1+
Blank	3½	2	1½	1+	1+
Nuodex Zn(8%)	3½	3	2	1½	1+
Nopco-CVT	4	3½	2½	2½	1½
Oleic Acid	4	3½	3½	2½	1½
Nopco-1072	4	3½	3	2½	1½
Glaurin	4	2½	2	1½	1½
Vel	3½	2	1½	1+	1+
Zinol	4	3	2	1½	1½
Lecivit "F"	3½	2	1½	1+	1+

Note: One is good dispersion, four is bad flocculation, and two and three are intermediates.

DISCUSSION OF RESULTS

LINSEED OIL

The tabulated results of the effect of various dispersing agents on pigment concentration on sedimentation, and on dispersion as viewed by a microscope will be discussed for linseed oil and varnish vehicles respectively.

Only one dispersing agent, Nopco-1072, increased the pigment concentration of the paste or paint over that of the blank. The others decreased the pigment concentration of the paste and paint to varying degrees. While the order of effectiveness of the agents was not definite comparing the paste test to the paint test, a decided trend was obtained. Keeping in mind that the higher the pigment concentration the more effective the agent, a comparison of the efficiency of the agents compared to the blank was made. This comparison is shown in Figure 5 for the paste test and Figure 6 for the paint test.

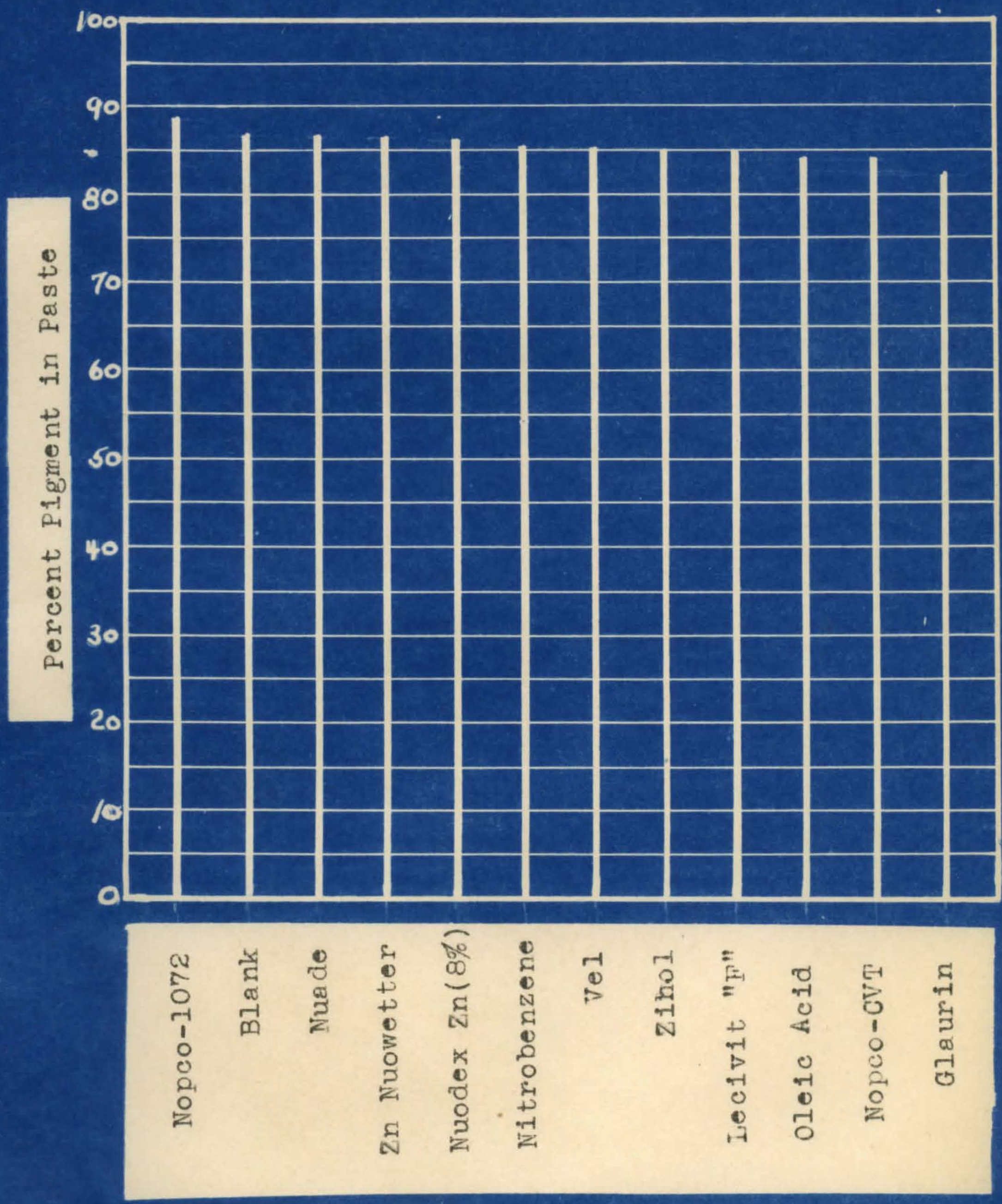

Figure 5 - Percent Pigment in Paste vs Agents

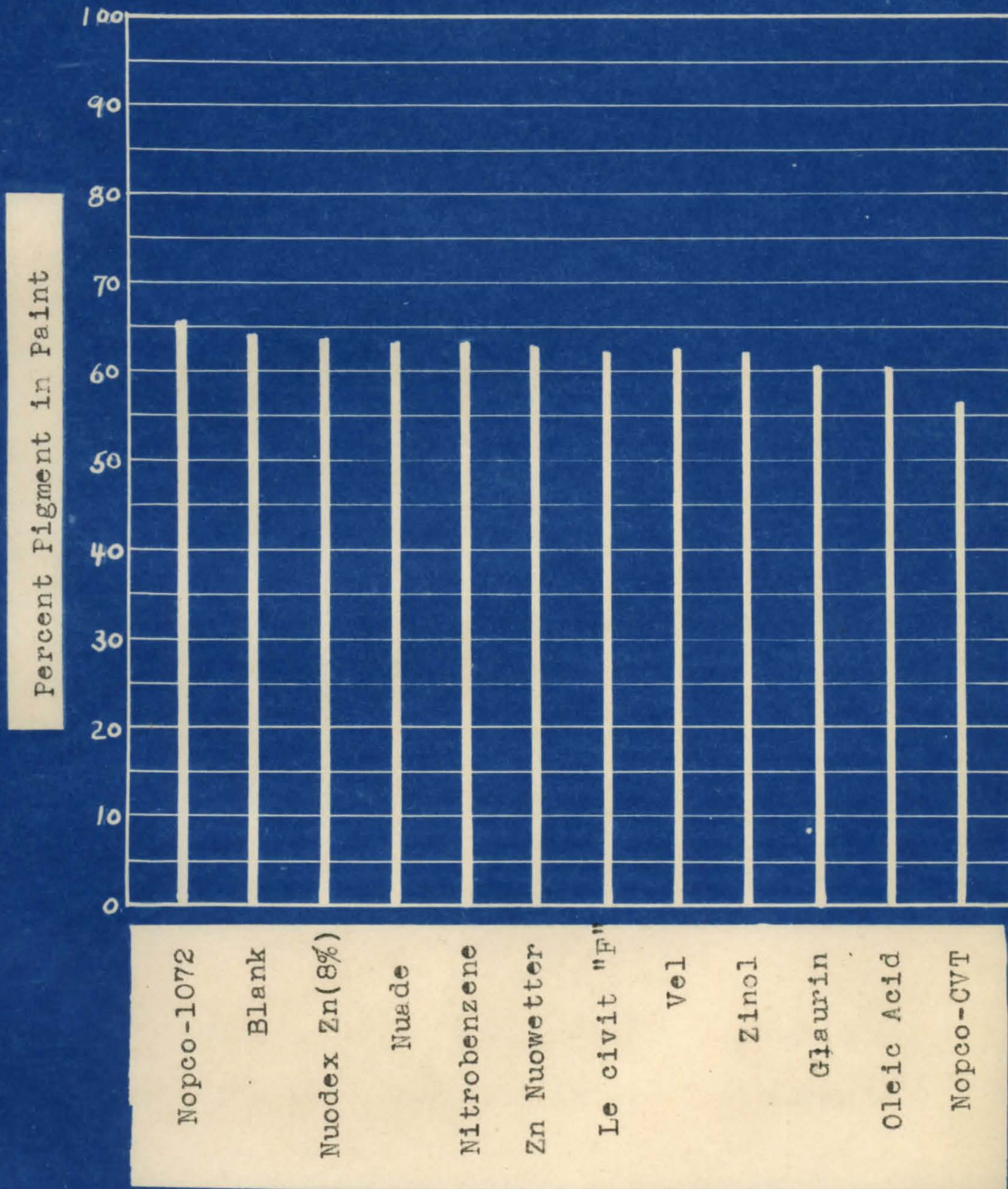

Figure 6 - Percent Pigment in Paint vs Agents

A comparison of the data obtained from the settling tests is shown in Figure 7. These data were obtained from Table IV. As the actual pigment that had settled was measured, an effective agent will show a lower ratio of pigment settled to total paint than the blank shows. Nuade and Nopco-1072 were in such good suspension that there was no appreciable cake, although the color deepened toward the bottom of the test tube. Zinol and Nopco-1072 also improved dispersion tendencies over the blank.

Zinol and the blank settled to an extremely hard cake, indicating that they were not too badly flocculated. The others, with the exception of Nuade, settled to a relative soft cake, indicating a higher degree of flocculation.

The data for the centrifuge tests were obtained by measuring the height of the pigment suspension, not the height of the actual pigment that settled. An effective agent, therefore, will have a high ratio of pigment suspended to total paint. A comparison of the efficiency of the agents, evaluated in this manner is shown in Figure 8. The ten minute centrifuge period was chosen because these data varied over a wider range than the forty minute period. For both the ten and forty minute tests only Nuade showed improvement over the blank.

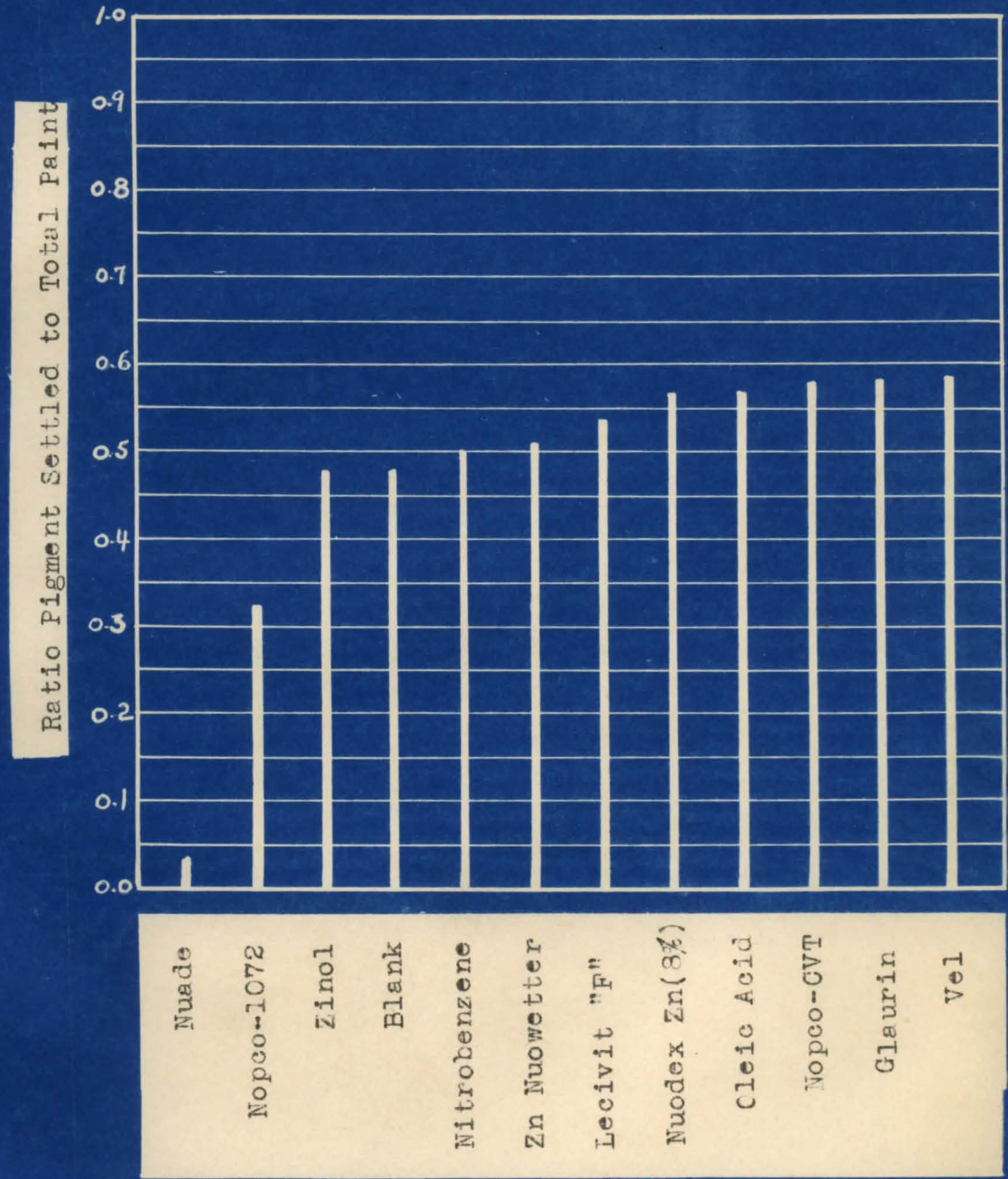

Figure 7 - Ratio Pigment Settled to Total Paint vs Agents

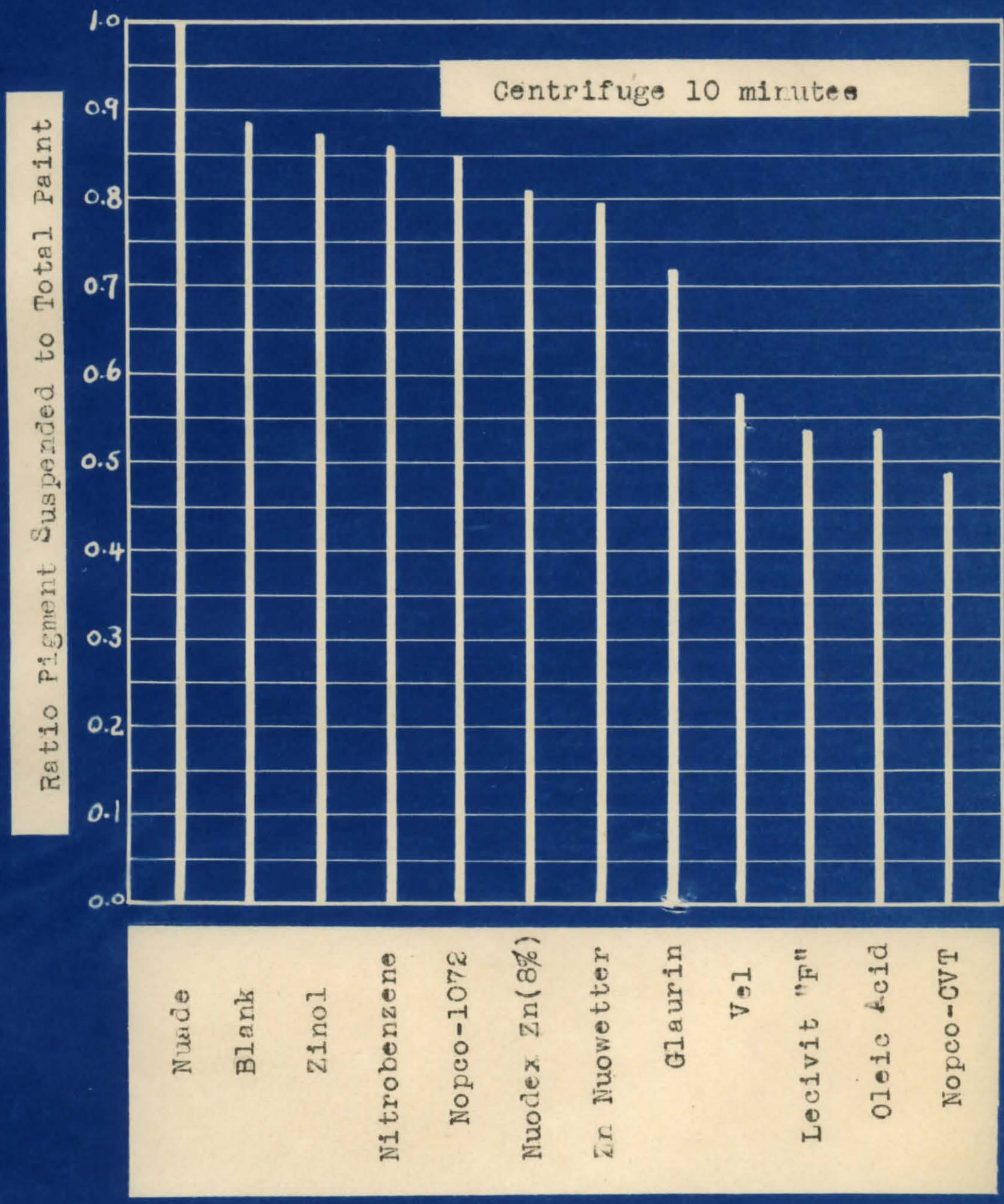

Figure 8 - Ratio Pigment Suspended to Total Paint vs Agents

This was a marked improvement in that no appreciable cake was apparent after three and one-half hours of centrifuging. For Nopco-CVT, Lecivit "F", and Vel the vehicle above the suspension was clear, indicating definitely poor agents. For Nuade, Nopco-1072, and Nuodex Zinc (8%) the vehicle above the suspension was cloudy, indicating relatively better dispersing agents. The intermediates showed varying degrees of cloudiness.

The results of observing dispersion under a microscope verified the results obtained in preceding tests. Nuade, Nopco-1072, and Nuodex Zinc (8%) showed less flocculation than the remaining agents, although the former showed very little improvement over the blank. These facts were also born out by observations after centrifuging, for these same agents were the first to show dispersion characteristics as the flocculates were thrown out.

VARNISH VEHICLE

Only one dispersing agent, nitrobenzene, increased the pigment concentration of the enamel, the others showing adverse results with reference to the blank. A comparison of the relative results of the agents, made with the blank, is shown in Figure 9.

The same procedure for evaluating results obtained by centrifuging with linseed oil was followed in evaluating the results of centrifuging with varnish. The results obtained, however, differenced in that a number of the agents proved superior to the blank. A comparison of the relative value of the agents, made with the blank, is shown in Figure 10. Comparison of the data for the ten and forty minute centrifuge periods shows that while the order of effectiveness of the agents was not definite, a decided trend was obtained. As shown by Table IX, the type of cake to which the enamel settled and the condition of the liquid above the suspension gave no helpful information.

A comparison of the microscopic observation, both shaken well and after centrifuging, showed relatively little results. All were flocculated when shaken well, with nitrobenzene, the blank, Nuodex Zinc (8%), Vel, and Lecivit "F" showing slightly less flocculation. These same agents were the first to show dispersion characterists as the flocculates were thrown out.

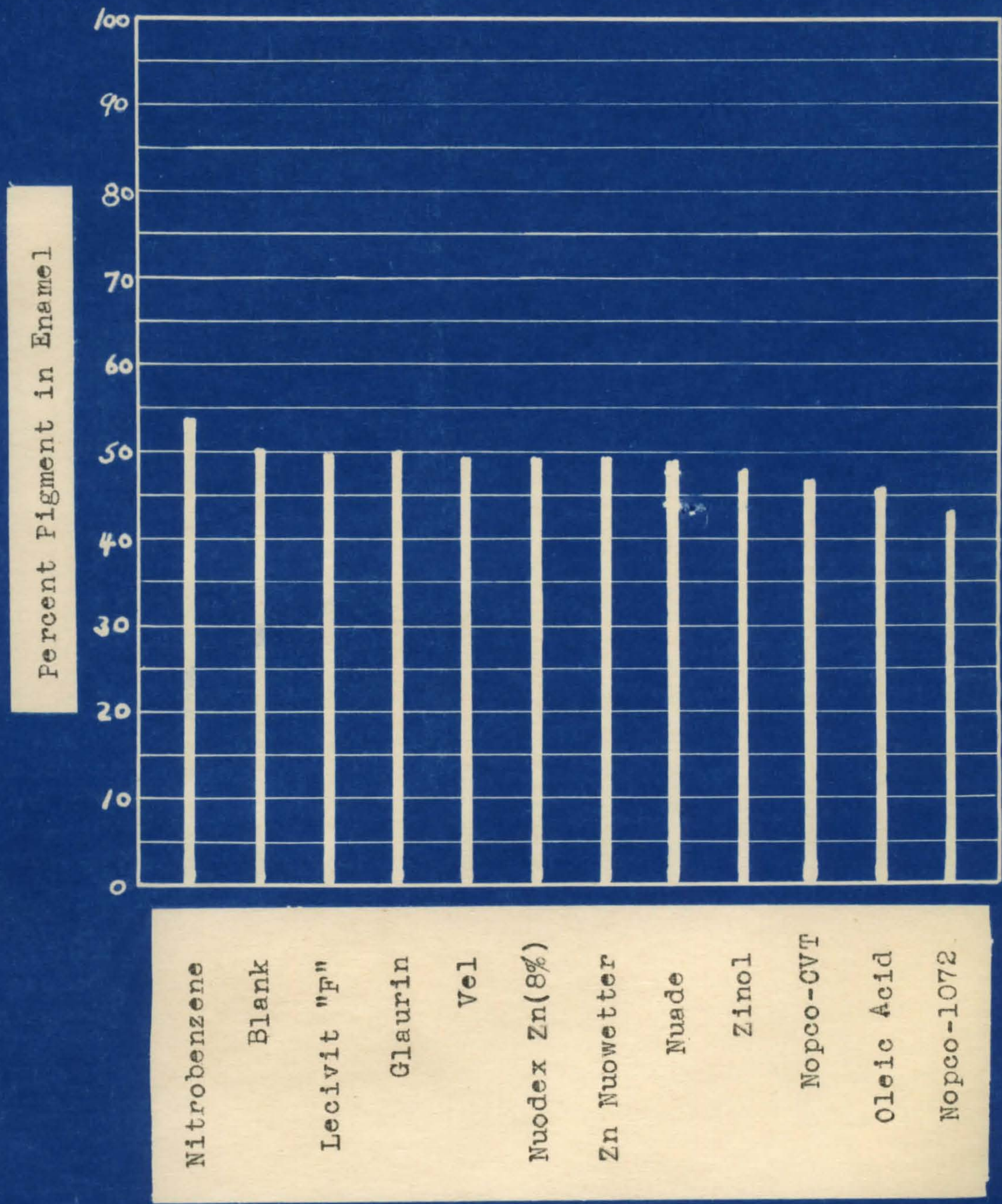

Figure 9 - Percent Pigment in Enamel vs Agents

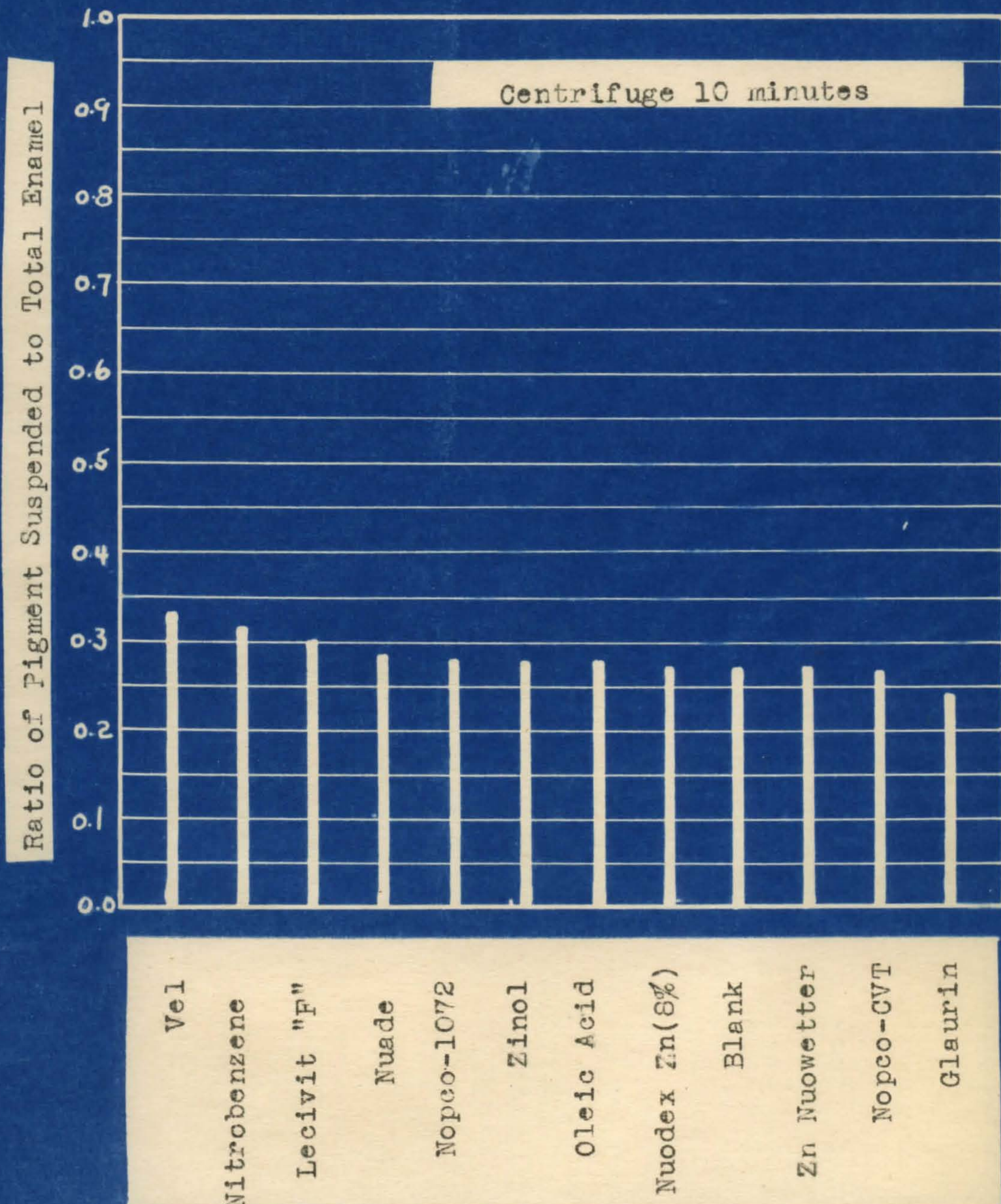

Figure 10 - Ratio Pigment Suspended to Total Enamel vs Agents

C O N C L U S I O N

Observation of the results of evaluating the dispersing agents by various methods, shown in Figures 5 through 10, lead to the following conclusions:

(1) In both linseed oil and varnish vehicles the method of evaluating showed that the degree to which an agent affected pigment dispersion, either positively or negatively, was comparatively consistent. While the order of effectiveness of the agents was not definite for the different methods, a definite trend was obtained.

(2) Test results showed that the degree to which an agent affected dispersion in linseed oil had no correlation with the degree to which an agent affected dispersion in the varnish vehicle.

(3) With linseed oil vehicle, only the agents Nuade and Nopco-1072 increased pigment dispersion, the others showing adverse results with reference to the blank.

(4) The agent nitrobenzene, when tested in varnish vehicle, was the only agent that aided pigment dispersion for all the methods of testing. Sedimentation tests and microscopic examination in this vehicle indicated that several agents aided, or at least had no adverse results on pigment dispersion.

It is suggested that this investigation is just a starting point for further work on the dispersion of cadmium pigment in paint and varnish vehicles. Only eleven dispersing agents were tested, and the effect of these on the properties of paint and enamel did not vary enough for any complete conclusions.

Although no operative dispersing agent was found, several existing methods of evaluating dispersing agents were utilized and one new method was developed.

A C K N O W L E D G E M E N T S

This investigation was made possible by a fellowship sponsored by the Louisville Paint, Varnish, and Lacquer Association. The author wishes to express his sincere thanks and appreciation for this fellowship.

The author wishes to thank Mr. H. L. Beakes and the Kentucky Color and Chemical Company for the valuable suggestions and information rendered, and the materials and facilities donated.

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V I T A

VITA

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