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SUBJECT

PHTHALATED WHITE PIGMENTS

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PIGMENTED WHITE PIGMENTS

l Statement:

This problem of chalking of titanium dioxide is not new. That this l is inherently a chalking pigment is well known. However, a new phase of oblem has arisen. There has appeared on the market titanium dioxide which is so excessively in comparison with previously supplied material that its use, same formula and in the same proportion, is attended with disastrous ts.

The producers of titanium dioxide offer no explanation for the enon, nor will they disclose any change that might have been made in produc- procedure which might be its cause.

No one has yet been able to distinguish between various titanium ides as to their chalking tendencies, either through chemical analysis or by of microscopic examinations. Actual exposure is still the only means at hand. this method is too slow for control purposes is evident.

The inherent danger of the situation is apparent. Wide variation of lking tendencies of titanium dioxide, even the product of the same manufacturer, been reported. No short method of test for distinguishing a titanium dioxide will chalk excessively from one that will not has yet been found. Then it advisable to study the chalking properties of all the various titanium diox- from all the domestic producers now on the market to devise a treatment for ifying the chalking tendencies of the pigment. By discovering the most effective d of treatment, we may be able to arrive at the explanation for the excessive lking of the material.

Briefly stated then this problem is to determine an effective method reducing the excessive chalking of titanium dioxide.

...ium Dioxide:

...normal process of chalking is familiar to all who have observed ...ing over its lifetime. The excessive and rapid chalking reported ...ide present certain aspects which differ from the normal process. ...ing thing about the phenomenon is the rapidity with which it takes ...

...This extremely rapid chalking, which is said to take place within ...eeks after exposure of the films, is described by observers as ...ools chalking first show tiny water spots after the sun and rain ...e tiny water spots rapidly spread and run together into a mass ...

...that titanium dioxide is a chemically inert pigment is well known. ...ed in the use of the material is acquainted with its poor wettabil- ...igment is both chemically inert, as is titanium dioxide, and of poor ...weak bond between pigment and vehicle results and the effect of air ...the film is pronounced. A very slight change in process of manu- ...easily produce great exaggeration in a characteristic probably al- ...ajor line.

...Furthermore, titanium dioxide is a calcined pigment. No doubt then ...particle of titanium dioxide, in the dry pigment, is enveloped by a ...sorbed to the surface. The existence of such films are discussed and ...facts set forth in proof by many authors. The influence of this film on ...the solid is strong. Bancroft (1) and Walker, Lewis, and McAdams (2) ...freely on this subject. Accepting as a fact the existence of this gas ...the particle, we may hypothecate an explanation of the behavior of the ...during and grinding with vehicle in the usual manner, it may be possible ...ment is over established between pigment and vehicle. The aggregates of

broken down and the pigment dispersed. Nevertheless each particle retains its gas envelope. When a film from such a dispersion is exposed ...le - gas film - pigment system holds the pigment loosely.

Then mechanism of the rapid chalking may be explained as follows: A ...riment outlined by Hoffman and reported by Bancroft (3), serves to estab- ...fact that titanium dioxide is a hydrophilic pigment. On exposure of the ...ribed above and when the film comes in contact with water, the titanium ...comes wet with water which displaces the gas envelope due to the greater ...for the water and the TiO_2. Once the water has penetrated the film the ...r bond is further weakened by the action of water and ultra-violet light. ...lm dries again, the surface now contains free TiO_2 which appears as

The first thought that occurs in order to strengthen the bond between ...ment and vehicle in the film is to remove the gas envelope in order that the ...system pigment-vehicle without the intervening gas might be established. ...g process would seem to offer such means. In this process the titanium ...uld first be wet with water, serving to displace the gas envelope, and ...ter would be displaced by the varnish vehicle. Under such treatment a ...ond will be established between pigment and vehicle. The value of our ...ll be proven by the comparative chalking rate of films prepared from paints ...two methods.

A second factor of no mean importance is the destructive action of ...et light on the films. Then it seems reasonable that if the film be ...rom ultra-violet that the excessive chalking may be prevented. A means of ...has been devised by H. A. Gardner (4). He says in part: "Titanium ...ppears to be of special interest because of its rather unique property of ...the chalking properties of other pigments, such as titanium oxide. When

er cent is precipitated upon a batch of titanium-barium pigment, rovement in weathering properties is noted.

The most active factor in destroying protective coatings is ultra- Pigments which transmit this light allow it to destroy the linseed binder in which the pigment is ground. On the other hand, if paints nts which do not transmit substantial amounts of ultra-violet light, ance and tint retention should be good - - - - - - . Most of the com- ed white opaque pigments transmit large quantities of ultra-violet least in certain wave lengths. On the other hand, the phthalate pigments ther none or extremely low amounts of such light."

Gardner describes a method whereby pigments may be coated with the reaction, in the presence of the suspended pigment, of sodium and the desired metallic salt. He suggests titanium phthalate as one of effective of the phthalates which he has investigated. The similarity of ion of maleic acid to phthalic acid make the maleates of interest in the

The third method by which the excessive chalking of the titanium di- be reduced is a familiar one. That is, by diluting the titanium dioxide hite pigments with little chalking tendency. Antimony oxide is widely purpose. Two new pigments which offer possibilities in this respect ently introduced lead titanate and zinc titanate.

The properties of lead titanate are discussed at length by D. W. 5). He states the pigment has high resistance to chalking, absorbs light 100% and imparts its characteristics to mixed pigments when it 20% or more of the mixture.

Zinc titanate is a comparative newcomer, whose properties have not determined. It is reported as a non-chalking pigment and is thus of this work.

The following ten titanium dioxide pigments were chosen for inves-

Grade	Producer
MO	Titanium Pigment Co.
LC	"
Special Experimental Non-Chalking	"
FF	Krebs Pigment & Col. Co.
LO	"
LW	"
SD Standard	American Zopaque Co.
SD Low Oil	"
GD Water Dispersible	"
Experimental	The Burgess Laboratories

Dioxide

Those pigments were given the treatment shown in the following
produce a white paste with pulping varnish. This vehicle, which is a
ceryl phthalate varnish was chosen because it is compatible both with
and lacquer formulation. The varnish is composed of 40% non-
mixed thinner in which mineral spirits predominates. The body is

From these pastes synthetic enamels on a typical Kem Automotive for-
ers on a low cotton automotive formula, were made. These enamels and
sprayed on panels using the recommended finishing schedule for each
The panels were sent to Miami, Florida, for exposure and weekly

reatment:

rgment	Pulped	Ground	Phthalated Pulped	Maleated Pulped
Titanium Dioxide		X		
-10	X	X		
1-10	X	X	X	
ring Titanox	X	X		
t	X	X	X	X
E	X	X	X	X
0	X	X		
d.	X	X		
10	X	X		
0	X	X		

reatment

ion:

The treatment for the phthalation of the titanium dioxide consisted to a water suspension of titanium dioxide a solution of sodium phthalate nder continuous agitation, a solution of titanium sulphate. The sodium and titanium sulphate were added in stoichiometric quantity to produce 5% phthalate based on the quantity of titanium dioxide being treated.

pension of Titanium Dioxide:

In order that the titanium dioxide should be well wet and that all should be broken up, 1000 gms. TiO_2 was put in the experimental pulper his water was added slowly to form a stiff paste. This paste was allowed roughly and then diluted with water and transferred to a twelve liter r. Water was added to a total volume of ten liters and the suspension ted.

ate Solution:

41.7 gms. phthalic anhydride was dissolved by heating in 800 cc
gms. of NaOH was dissolved in 200 cc water. The two solutions were
esultant sodium phthalate solution was faintly alkaline to litmus.
ion was then added to the suspension of 1000 gms. TiO_2 in water.

lphate Solution:

The titanium sulphate used in this work analyzed 21.34% TiO_2.
$(SO_4)_2$ were put in 1 liter of water and agitated from time to time. A
below 20° C. aids solutions without hydrolysis. Eight hours were re-
a clear solution, while overnight gave better results.

tion of the Phthalate:

To the suspension of TiO_2, to which the sodium phthalate solution
dded, the titanium sulphate solution was added dropwise and under con-
itation.

, Washing:

After the precipitation of the phthalate the pigment was permitted
vernight. The supernatant liquid was tested for complete precipitation
anium and decanted. The pigment was diluted largely with water, agitated
liquid filtered. The cake was washed free of SO_4 ion with water and
pulping.

The treatment for maleation of the pigment was identical to that
lation. Maleic anhydride took the place of phthalic anhydride. The
used, based on 1000 grams TiO_2 were as follows: 72 gms. $Ti(SO_4)_2$;
leic anhydride; 30.7 gms. NaOH.

...cess:

Considerable doubt arose that a sufficiently well wet titanium di- could be produced by simply adding water to dry TiO_2. It can readily be ...t is essential that each individual particle of TiO_2 must be wet with ...he aggregates be broken up in order that when the pulping operation is ...ut, a complete dispersion of the TiO_2 in the vehicle will be obtained. It ...his in mind that the action of wetting agents on the TiO_2 was studied. ...tubes small quantities of dry TiO_2 were placed. To these tubes water ...of various wetting agents were added. The agents tried were: Avrol, ... Daxad and others. The tubes were shaken until the TiO_2 was well sus- ...the liquid. A tube containing only TiO_2 and water without any wetting ...as used for comparison. No beneficial action of the wetting agent could be ...the rate of settling of the suspension in the tubes.

It was then decided to try pulping the TiO_2 by simply wetting the ...with water and then using this as the wet cake and proceeding with the ...m. After correction of a few minor details, it was found that a satis- ...y dispersed TiO_2 paste could be obtained in this manner.

On preliminary experiments in pulping the TiO_2 cake, prepared as ...ith pulping varnish, it was found that the pulping varnish would not flush ...from the mass. The water was held most tenaciously by the pigment. The ...flushing agent was resorted to. A 50% solution of turkey red oil in water ...to the mass and later an equal portion of a 50% solution of basic lead ...in water. Under this treatment the water was separated from the pigment on ...of varnish and could be poured off.

Then the normal procedure for the pulping operation was as follows:

To prepare this pulp 1000 gms. dry TiO_2 was put in the 1 gallon size
00 cc. water was added slowly, taking the pigment through a very stiff
in order that the maximum effect of the mechanical work of the agitators
obtained. This cake was dumped from the pulper and the operation repeated.
of pulping varnish was weighed out. The varnish was added to the pulp in
slowly until approximately 300 gms. had been used. Now the flushing
added. First 25 gms. of turkey red oil solution, then later 25 gms.
acetate solution. Agitation was continuous throughout the entire opera-
the water had broken out and was clear it was poured off. Water pulp
varnish were added in alternate portions until all of both were used. As
freed it was poured off. Now all the water was removed from the mass by
ication of heat and reduced pressure. When there was no further evolution
le from the pulper, the vacuum was released and cold water replaced steam
lse bottom of the pulper. The mass in the pulper was thinned with xylol
o the lost volatile from the varnish. The resulting paste was passed
three-roll laboratory size mill. The rolls were loosely set. This had for
se the smoothing out of all lumps rather than that of dispersing the pig-

A table is given herewith showing comparative behavior of the various
dioxides on pulping.

Treatment	Qty.	Water for Pulp	Water Flushed Out	Pulping Varnish	Turkey Red Oil Soln.	Basic Lead Acetate Soln.	Xylol
	gms.	cc	cc	gms.	gms.	gms.	
LO None	2000	1000	725	1060	25	25	618
LO "	2000	1000	625	1060	25	25	618
LM "	2000	1000	700	1060	37.5	37.5	618

Treatment	Qty. gms.	Water for Pulp cc	Water Flushed Out cc	Pulping Varnish gms.	Turkey Red Oil Soln. gms.	Basic Lead Acetate Soln. gms.	Xylol
None	2000	1000	730	1060	50	50	618
"	2000	1000	600	1060	25	25	618
"	2000	1000	650	1060	25	25	618
"	2000	1000	675	1060	25	25	618
"	2000	1000	575	1060	25	25	618
Phthalated	1500	990	750	795	0	0	477
"	2000	1400	960	1060	0	0	618
Maleated	1000	490	250	530	12.5	12.5	309
"	1500	1170	1000	795	18.75	18.75	463

With the exception of the pigments hereafter discussed, the pulping ...irely normal. The water broke from the mass with the same ease and with the ...tity of flushing agent.

In the case of the water dispersible titanium dioxides, Ti Pure LW ...e GD, abnormal behavior was encountered.

On putting the dry Ti Pure LW in the pulper and adding the water ... pigment set in such a hard, rock-like mass that the machine stalled. ... procedure i.e. putting the water in the pulper and adding the pigment ...reto resulted in a thin, fluid dispersion of TiO_2 in the water. At the ...ent concentration all the other pigments gave pastes. Pigment from this ...persion attached itself to every metal surface with which it came in contact. ...tanding, a film very much like a paint skin formed on the surface.

...hen varnish was added to begin the pulping process, the mixture ...ity and became thick. Its appearance at this stage was just like ...her pigments. However, the water would not break from the mass as ...as much again of the pulping agents had to be added to get a normal

...The Zopaque GD formed a normal water pulp with the same quantity of ...the same method as with the other pigments. However, it resisted ...ously. Double the normal quantity of pulping agents was necessary to ...factory break.

...The pigments which had been treated with titanium phthalate were ...no pulping agent was necessary to pulp them. They broke nicely on ...rnish to the filter cake in the pulper.

...In the case of the pigments treated with titanium maleate, pulping ...al quantity was necessary to bring about a break.

...In order that the bases prepared from the dry pigments mixed and ...vehicle might be comparable with the pulped bases, the same propor- ...and vehicle was used. The formula is:

2000 gms. Titanium Dioxide

1060 " Pulping Varnish

...each case the pigment was well mixed with the vehicle and ground ...laboratory size, mill to a 4P grind.

...ts:

...The pigments used in blending with the TiO_2 in the enamels and ...itanate, antimony oxide, and lead titanate were mixed and ground ... It was the original intention to pulp these pigments also. Pre- ...nts showed this was impractical. The same technique as that used

dioxide was tried. On adding the vehicle to the water pulp the
from the water immediately and in a poorly dispersed and agglomerated

A simple test to forecast the behavior: Test tubes were prepared
two phase liquid, water on the bottom and toluol above. In this,
of the various pigments were dropped. Titanium dioxide immediately
ater phase, antimony oxides remained in the toluol phase and zinc
ined at the interface. From this we may reason that while titanium
decidedly hydrophilic, the others are definitely not. Thus while a
ater pulp was prepared by mixing TiO_2 and water that the other pig-
ot wetted by the water and hence on pulping, a poorly dispersed base
This naturally led to an investigation of wetting agents for the non-
pigments. A few attempts were unsuccessful and in order to expedite
idea of pulping zinc titanate, antimony oxide and lead titanate was
abandoned.

As in the case of the titanium dioxide these pigments were ground
manner and on the following formulae:

2000 gms.	Zinc Titanate	
1060 "	Synthetic Medium Oil Grinding Varnish	
2000 gms.	Antimony Oxide	
1060 "	Synthetic Medium Oil Grinding Varnish	
2000 gms.	Lead Titanate	
500 "	Synthetic Medium Oil Grinding Varnish	
560 "	Synthetic Medium Oil Grinding Varnish	

...ite Enamels:

The synthetic enamels for exposure were prepared by blending the ...shown in the formula below, in which titanium dioxide was the only white ...

77	gms.	Titanium Dioxide base
140	"	Lamp black tinting base
40	"	Chrome orange tinting base
99	"	(2118) Synthetic CWO Mod. Oil Mixing Varnish
198	"	(2132) " Linseed " " " "
25	"	(4037) Lead Manganese Naphtenate Drier
12.5	"	(2247) Lead Manganese Cobalt Naphthenate Drier

In the enamels containing the blended white pigments, 33% of the ... pigment base was substituted for titanium dioxide base.

...ion of Lacquers:

The lacquers were prepared by blending on the following formula in ...hich titanium dioxide is the sole white pigment:

260	gms.	Bone Black Lacquer Base
42	"	Titanium Dioxide base
200	"	½ Sec.N.C. Solution, 25% Solids
14	"	Glyptal
20	"	Butyl Acetate
40	"	Resin Solution in Toluol, 60% Solids
172	"	Glyptal Solution, 60% Solids
20	"	Butyl alcohol
10	"	Methyl Ethyl Ketone
90	"	Lacquer Thinner

In the case of the lacquers containing the mixed white pigments, ...anium dioxide base was replaced with the modifying pigment base.

...f the Exposure Panels:

The panels on which the exposures were made are 8"x24" crimped edge ... They were carefully cleaned of all grease and sprayed with one coat ... Rex 43803 reduced 50% with Kem Reducer #75. This coat was permitted ...urs, sanded lightly and the samples applied.

The synthetic enamels were reduced 33-1/3% with Kem Reducer #75. ...y was applied by spraying.

The lacquers were sprayed on two coats, 30 minutes between coats, ...duction with lacquer reducer.

The panels were exposed 45° facing South in Miami, Florida. They ... weekly for gloss retention and chalking.

The following table gives a resume of ... panels:

White Pigment	Treatment of TiO_2
Titanox A LO	Pulped
Ti Pure LO	Pulped
Zopaque LO	Pulped
Titanox A LO	Ground
Ti Pure LO	Ground
N. C. Titanox	Ground
Ti Pure LO	Maleated, Pulped
Titanox A LO	Phthalated, Pulped
Ti Pure LO	Phthalated, Pulped
67% Titanox A LO, 33% Antimony Oxide	Pulped

White Pigment	Treatment of TiO_2
(Cont'd)	
67% Ti Pure LO, 33% Antimony Oxide	Pulped
67% Ti Pure LO, 33% Antimony Oxide	Maleated, Pulped
67% Titanox A LO, 33% Antimony Oxide	Phthalated, Pulped
67% Ti Pure LO, 33% Antimony Oxide	Phthalated, Pulped
67% Titanox A LO, 33% Zinc Titanate	Pulped
67% Ti Pure LO, 33% Zinc Titanate	Pulped
67% Ti Pure LO, 33% Zinc Titanate	Maleated, Pulped
67% Titanox A LO, 33% Zinc Titanate	Phthalated, Pulped
67% Ti Pure LO, 33% Zinc Titanate	Phthalated, Pulped
67% Titanox A LO, 33% Lead Titanate	Pulped
67% Ti Pure LO, 33% Lead Titanate	Pulped
67% Ti Pure LO, 33% Lead Titanate	Maleated, Pulped
67% Titanox A LO, 33% Lead Titanate	Phthalated, Pulped
67% Ti Pure LO, 33% Lead Titanate	Phthalated, Pulped
MO Enamels -	
Titanox A MO	Pulped
Titanox A LO	"
Ti Pure FF	"
Ti Pure LO	"
Ti Pure LW	"
Zopaque Std.	"
Zopaque LO	"
Zopaque GD	"
Burgess TiO_2	Ground
Titanox A MO	"

White Pigment	Treatment of TiO_2
Enamels (Cont'd) -	
Titanox A LO	Ground
Non-Chalking Titanox	"
Ti Pure FF	"
Ti Pure LO	"
Ti Pure LW	"
Zopaque Std.	"
Zopaque LO	"
Zopaque GD	"
Ti Pure FF	Maleated, Pulped
Ti Pure FF	Phthalated, Pulped
67% Titanox A MO, 33% Antimony Oxide	Pulped
67% Ti Pure FF, 33% Antimony Oxide	"
67% Zopaque Std. 33% Antimony Oxide	"
67% Ti Pure FF, 33% Antimony Oxide	Maleated, Pulped
67% Ti Pure FF, 33% Antimony Oxide	Phthalated, Pulped
67% Ti Pure FF, 33% Zinc Titanate	Pulped
67% Ti Pure FF, 33% Zinc Titanate	"
67% Zopaque Std., 33% Zinc Titanate	"
67% Ti Pure FF, 33% Zinc Titanate	Maleated Pulped
67% Ti Pure FF, 33% Zinc Titanate	Phthalated Pulped
67% Titanox A MO, 33% Lead Titanate	Pulped
67% Ti Pure FF, 33% Lead Titanate	"
67% Zopaque Std., 33% Lead Titanate	"
67% Ti Pure FF, 33% Lead Titanate	Maleated, Pulped
67% Ti Pure FF, 33% Lead Titanate	Phthalated, Pulped

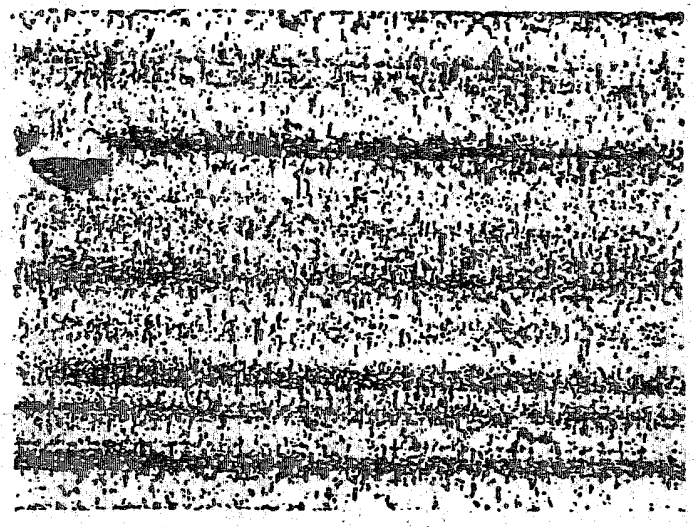

Plate 15. #254-A

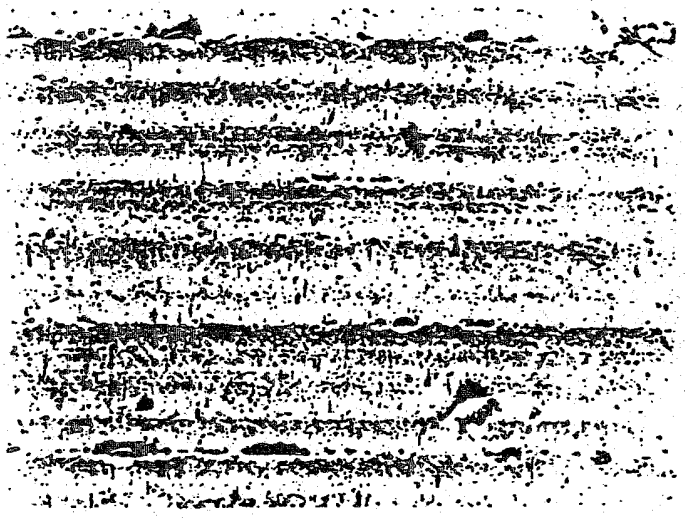

Plate 16. #254-B

This panel is very similar to #253, as would be expected from the
tion of DB 1752 for V 7669 as the soybean portion of the combination
2109).

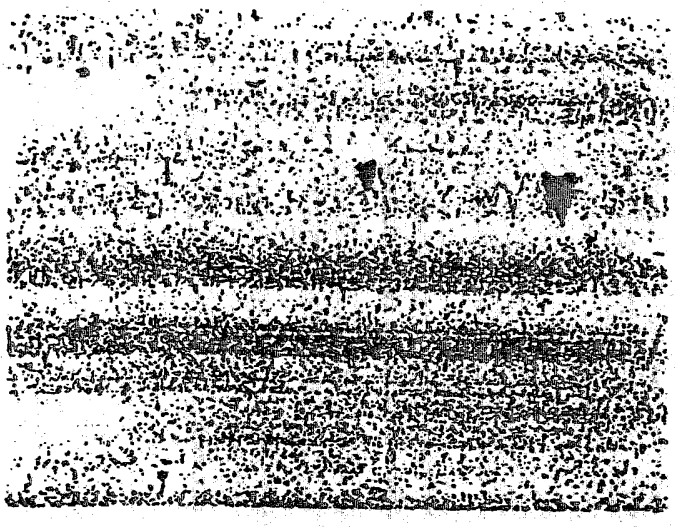

Plate 17. #256-A

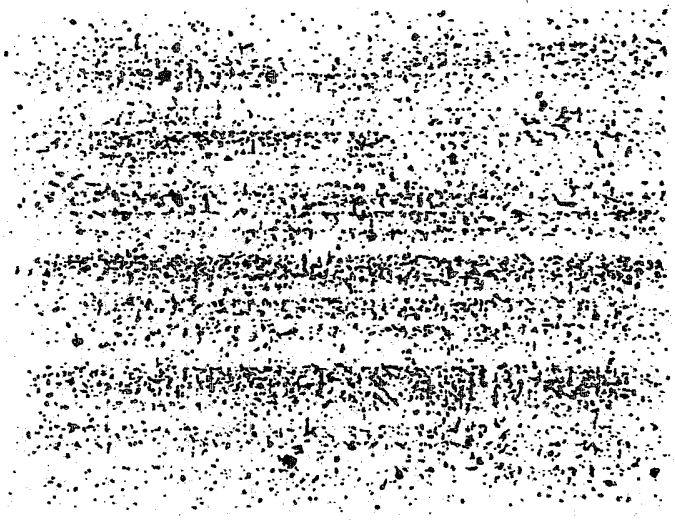

Plate 18. #256-B

Again the good durability achieved through the use of a soybean
lic vehicle DB 1752 is illustrated. This verifies the results shown in
252.

. From the above it appears very obvious that the high pigment-volume zinc oxide pigmentation was superior to the low pigment-volume titanium antimony oxide - zinc oxide pigmentation adopted later (and subsequently

).

of Results, Plans for Future Work:

As discussed elsewhere, we are elaborating on these studies of tion to include the present pigmentation and the substitution of titanium asbestine mixes and titanium dioxide - asbestine - mica for the Titanox original formula, maintaining high pigment-volume.

In order of durability from the standpoint of vehicle we must rate best, linseed-perilla intermediate, and fish oil inferior. Unfortunately cannot take full advantage of this information because soybean oil the drying, particularly under unfavorable conditions. We are particularly hered by lowered water resistance and increase of hydrophilic tendencies drying. This is very important in evaluating bulletin colors.

In order to take some advantage of the increased durability of the vehicle we are investigating a synthetic oil which is intermediate 7669 and (2109). This is V 7762 which is a 23.3 length synthetic oil, ed, 5 perilla, and 5 soybean.

Also, we will try a partial substitution of the soybean vehicle th phenolic resins to improve the drying, and to reduce the hydrophilic