ALLIED RESEARCH BULLETIN

Number RC 28

SUBJECT

DURABILITY STUDIES OF REX 45000 - KEM BULLETIN WHITE

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ALLIED RESEARCH LABORATORIES

CHICAGO, ILLINOIS

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DURABILITY STUDIES OF REX 45000 - KEM BULLETIN WHITE

oduction and Scope:

This report describes the results obtained from a series of expo- of experimental formulas of Rex 45000 - Kem Bulletin White. The variations nde changes in pigmentation and in vehicle composition. We believe that the er phase, that of studies of vehicle changes, give worth while information as he comparative durability characteristics of linseed-perilla combinations, oil, and soybean oil types of synthetic vehicles.

paration and Methods of Exposure:

The exposures were all prepared on 8" x 24" galvanized iron panels. first coat was Galvite Primer - Rex 26440, reduced 25% with mineral spirits dried 24 hours (in the laboratory). The second coat was the experimental 45000, reduced 12-1/2% with mineral spirits, and applied to the upper half of panel only. After an additional 24 hours of drying, an over-all coat of the imental Rex 45000 was applied. Thus we have in effect both the conventional coat and three-coat systems, acknowledging that a difference of drying appears he application of the final coat (48 hours on the primer between coats for coat system vs 24 hours between coats for three-coat system).

On each panel the "A" section is the three-coat area, and the "B" on the two-coat area.

The panels were placed on exposure, 45° south, on our Chicago expo- farm, on 8-20-36, and the exposures discontinued on 5-20-37, representing a of nine months' exposure, largely during winter months.

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lementary Report
ve Weeks' Panel Exposure

The condition of the panels carrying the synthetic enamels and
ers, made with the variously treated titanium dioxides, after six and twelve
exposure respectively at 45° facing south in Miami, Florida, is tabulated

ers

White Pigment	Treatment of Titanium Dioxide	Chalking 6 Weeks	Chalking 12 Weeks
Titanox-A LO	Pulped	None	Very slight
Krebs LO	"	"	Moderate
Zopaque LO	"	"	Very slight
Titanox-A LO	Ground	"	Slight
Krebs LO	"	"	"
NC Titanox	"	"	None
Krebs LO	Maleated Pulped	"	Very slight
Titanox-A LO	Phthalated Pulped	"	None
Krebs LO	Phthalated Pulped	"	Incipient
Titanox-A LO Antimony Oxide	Pulped	"	Very slight
Krebs LO Antimony Oxide	"	"	Slight
Krebs LO Antimony Oxide	Maleated Pulped	"	Barely perceptible
Titanox-A LO Antimony Oxide	Phthalated Pulped	"	Incipient

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White Pigment	Treatment of Titanium Dioxide	Chalking 6 Weeks	Chalking 12 Weeks
Krebs LO Antimony Oxide	Phthalated Pulped	None	Very slight
Titanox-A LO Zinc Titanate	Pulped	Incipient	Moderate, bad fading
Krebs LO Zinc Titanate	"	"	" " "
Krebs LO Zinc Titanate	Maleated Pulped	None	Incipient
Titanox-A LO Zinc Titanate	Phthalated Pulped	"	"
Krebs LO Zinc Titanate	Phthalated Pulped	"	"
Titanox-A LO Lead Titanate	Pulped	"	Moderate, bad fading
Krebs LO Lead Titanate	Pulped	Incipient	" " "
Krebs LO Lead Titanate	Maleated Pulped	None	Barely perceptible
Titanox-A LO Lead Titanate	Phthalated Pulped	"	" "
Krebs LO Lead Titanate	Phthalated Pulped	"	" "
Enamels			
Titanox-A MO	Pulped	Slight	Bad
Titanox-A LO	"	"	"
Krebs FF	"	"	"
Krebs LO	"	"	"
Krebs LW	"	"	"

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C Enamels (Cont'd)

White Pigment	Treatment of Titanium Dioxide	Chalking 6 Weeks	Chalking 12 Weeks
Zopaque Standard	Pulped	Incipient	Bad
Zopaque LO	"	"	Moderate
Zopaque GD	"	Slight	Bad
Burgess Exp.	Ground	None	Moderate
Titanox-A MO	"	Slight	Severe
Titanox-A LO	"	"	Bad
Non-chalking Titanox	"	None	Incipient
Krebs FF	"	Slight	Severe
Krebs LO	"	"	"
Krebs LW	"	Moderate	"
Zopaque Standard	"	Slight	Moderate
Zopaque LO	"	"	Bad
Zopaque GD	"	"	"
Krebs FF	Maleated Pulped	None	Moderate (fading)
Krebs FF	Phthalated Pulped	"	Moderate
Titanox-A MO Antimony Oxide	Pulped	Incipient	Bad
Krebs FF Antimony Oxide	"	"	"
Zopaque Standard Antimony Oxide	"	None	Very slight
Krebs FF Antimony Oxide	Maleated Pulped	"	" "

Panels (Cont'd)

White Pigment	Treatment of Titanium Dioxide	Chalking 8 Weeks	Chalking 12 Weeks
Krobs FF Antimony Oxide	Phthalated Pulped	None	Moderate
Titanox-A MO Zinc Titanate	Pulped	Incipient	Bad
Krobs FF Zinc Titanate	"	Very slight	"
Opaque Standard Zinc Titanate	"	None	Moderate
Krobs FF ZINC TITANATE	Maleated Pulped	"	Incipient
Krobs FF Zinc Titanate	Phthalated Pulped	"	"
Titanox-A MO Lead Titanate	Pulped	Slight	Severe
Krebs FF Lead Titanate	"	Incipient	Moderate
Opaque Standard Lead Titanate	"	None	Severe
Krobs FF Lead Titanate	Maleated Pulped	"	Slight
Krobs FF Lead Titanate	Phthalated Pulped	"	"

ins practiced in this investigation is ineffective in deferring the
of the TiO_2 or in lessening its severity.
ion or malcation, i.e. surface coating the pigment with titanium
te or titanium maleate respectively, is quite effective in deferring the

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lking of TiO_2 and in lessening its severity both in synthetic enamels and lacquer.

ifference in chalking tendency of the TiO_2 pigment from different sources pparent. In order of chalking they are as follows: Zopaque, least; nox-A, intermediate; Krebs, most. The difference is too slight to offer great margin of safety. The Burgess Experimental TiO_2 is quite resistant halking, but lacks other desirable pigment properties.

Zinc titanate and lead titanate behave in a most unsatisfactory manner in uer. They apparently induce excessive fading and in 33-1/3% admixture with reated TiO_2 do not affect chalking rate. In this same per cent admixture phthalated or maleated TiO_2 behavior is more normal.

titanate, zinc titanate and antimony oxide in 33-1/3% admixture with reated TiO_2 offer little or no protection in deferring or lessening chalking.

ime:

In order to determine the effect of the phthalated pigments and lead titanate on drying time of the synthetic enamels, the following ere chosen:

Synthetic enamels made for this work on March 18, 1937, and which in storage for five months. The white pigments in the enamels are as

1. Untreated Titanium Dioxide
2. 5% Phthalated Titanium Dioxide
3. 5% Maleated Titanium Dioxide
4. Special Non-chalking Titanox-A
5. 33-1/3% Lead Titanate, 66-2/3% Titanium Dioxide
6. 33-1/3% Zinc Titanate, 66-2/3% Titanium Dioxide

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These enamels were sprayed one coat on steel panels and compared freshly prepared enamel, made on the same formula and in which the white was untreated titanium dioxide, for drying time.

No difference was apparent in the drying rate of the seven enamels.

Work:

In order to test fully the value of phthalation of titanium dioxide, following pigments will be prepared, made into enamels and lacquers on the given in the first report on this subject, sprayed on panels and exposed do.

1. Control, untreated Titanox-A
2. Titanox-A - 2½% phthalation
3. Titanox-A - 5% phthalation
4. Titanox-A - 10% phthalation
5. Titanox-A - 15% phthalation
6. Titanox-A - treated only with phthalic anhydride

There will be included with these exposures panels prepared using non-chalking Titanox-A, prepared by The Titanium Pigment Company, the method ment of which has not been disclosed.

Further reports will follow.

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ALLIED RESEARCH BULLETIN

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SUBJECT

AFTER-BODYING OF LITHOPONE PAINTS
AND ENAMELS

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Discussion

After-bodying of Lithopone paints is closely related to the surface ...y of the Lithopone particle and presents a type of phenomena somewhat ...from that usually associated with normal consistency values.

Today under the concepts built up by physicists this latter type ...ivity is now considered to be both physical and chemical. The forces ...ntrol surface reactivity operate in addition to those of a more purely ...l character, usually associated with wetting phenomena and upon which Litho- ...sistency evaluations have been generally based.

The study of surface phenomena is in its infancy, but sufficient ...are known to serve as guides in determining the suitability of Lithopones ...ous purposes. Wettability and consistency phenomena are discussed in Re- ...Bulletins 11 and 12 - "Wetting and Dispersing Agents in Paint Formulation," ...Procedure for Evaluating Lithopone as Regards Consistency."

Several designations have been used to describe surface reactivity ...ted to Lithopone, among which "surface attraction," "adsorption capacity," ...ysical chemical attraction" have been selected as most self-explanatory. ...ons of simplicity this type of reactivity will be expressed by numerical ...designated as the "P-C" factor (P-C = physico-chemical). This reactivity ...ieved to be related to a physical condition of the surface of the Lithopone ...rather than to a distinctly chemical condition. This physical condition ...ely related to the character of the porosity of the surface and those for- ...ch operate in and on micro-cellular structures as well as to the atomic ...s in the surface molecules.

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Conditions which favor the production of a finely particled Litho- increased surface areas - with increased surface porosity of which the high ency Lithopones are typical, produce Lithopones of high surface reactivity, etting characteristics. Hence over-calcined Lithopones of larger par- ize are generally of low surface reactivity and good wetting qualities. llowing table shows typical "P-C" or surface reactivity factors for several of Lithopone as determined by the standard procedure given under a subse- ption.

Table I

"P-C" Factors According to Lithopone Grades

Lithopones		"P-C" Factor
Low consistency	L, LL and low M ranges	3.5 to 5.0
Medium "	High M, R and S ranges	5.0 to 6.0
High "	H ranges	6.0 to 9.5

In the middle consistency ranges a "P-C" factor in excess of 6.5 expected to show after-bodying characteristics with sensitive vehicles, hose which contain polymers not far removed from the gelation point.

Soap treated Lithopones - those which have received a treatment tty acid soaps of complete or partial neutrality, usually have a surface ity approaching zero, since the attraction has been neutralized by the g agent. Therefore, it is possible to reduce the surface reactivity of a ithopone to any desired point by the addition of definite amounts of such to the Lithopone "in the wet."

It has been observed that Lithopones of high pH value can show a wer surface reactivity or "P-C" value than would be expected from their alinity and the reverse condition has also been noted.

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ing Due to Surface Reactivity

The general premise, that maximum Lithopone production and consump-
ld be directed to three types of Lithopone - a low, medium, and high con-
should be kept continually in mind by the technical men associated with
production and by the paint formulators and superintendents, if special
grades are to be reduced to the minimum.

To meet this plan adequately, these three grades of Lithopone must
"general purpose" type, which will not react to an appreciable extent
sitive" vehicles, possess excellent mixing and grinding characteristics
paint consistencies in line with the established "A" and "B" consistency
Therefore, above all, a "general purpose" Lithopone must be relatively
rface reactivity or "P-C" factor.

The high consistency Lithopones constitute a partial exception, as
iable degree of reactivity is associated with increased consistency.
itself limits their general usage and makes it necessary that with such
es, the "P-C" factor be closely controlled.

Poor wetting Lithopones, i.e., those having a high adsorption
y, may behave normally as to their consistency characteristics in those
which possess a safe solvency balance between the various polar constit-
emselves and also between the non-polar and polar constituents. (Mineral
typically non-polar, fatty acids the most active polar, and oils according
ee of polymerization of varying polarities).

Such poor wetting Lithopones may exhibit normal "A" and "B" con-
y factors, but if used with a "sensitive" or unbalanced vehicle, i.e., one
o the threshold of gelation, may show an abnormal increase in consistency,

probably exhibit marked after-bodying characteristics, resulting in customer complaints unless caught by the paint factory personnel.

The use of these "sensitive" or unbalanced vehicles in paint factory practice has now become so widespread, that an appreciable degree of reactivity must be permitted in deliveries of "general purpose" Lithopones, if paint factory customer complaints are to be avoided.

Vehicles may be "sensitive" to surface reactive Lithopones as to viscosity either initially, or on storage, for a number of reasons, most of which are related to phases of polymerization and solvency. A reactive Lithopone may adsorb and remove from solution in the vehicle, a sufficient quantity of the most polar constituents - fatty acids of varying degrees of polymerization - and deposit as primary and secondary envelopes on and adjacent to the pigment particle surfaces, to reduce the solvency of the high polymers in the balance of the vehicle to the "gelation point" causing the paint to thicken.

This preferential adsorption and orientation of these polar bodies around the pigment particles is a time reaction and hence may become known as after-bodying.

Again, a high concentration of a non-polar constituent in a vehicle of the above type, as is frequently the case in traffic zone and flat wall paints is found to produce after-bodying with reactive Lithopones for similar reasons.

The formation of enormously high polymers of low solubility, such as are found in large quantities in the highly heat-bodied oils (10 minute to 20 minute Sward-Stormer tube) are not only a source of high initial consistencies with surface reactive Lithopone pigments but are also a frequent cause of after-bodying.

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China Wood Oil Varnishes in which the oil has been highly polymer-

Phenolic Resin Varnishes in which the resin has not been completely

frequently show after-bodying troubles with surface reaction Lithopones.

pplications of the Above Principles

The following illustrations indicate how the reactivity or "P-C" Lithopone influences the consistency of paint factory productions when of the types discussed in the above caption are used.

Two production lots of Lithopone of similar wettability character- shown by the following "A" and "B" factors but with widely differing ctors were tried in a typical traffic zone paint.

Table II

Lithopone Characteristics

"P-C" Factor	"A" Factor Initial	"A" Factor After-Body	"B" Factor Initial	"B" Factor After-Body
11.7	19.2	+ 3.2 sec.	21.8	- 0.4 sec.
5.7	18.9	+ 0.3 "	20.2	+ 0.4 "

The Lithopone with the high reactivity of 11.7 gave excessive odying of the traffic paint in question, while the other Lithopone having factor of 5.7 showed normal initial body and the paint maintained that on storage in the can.

The effect of a highly surface reactive Lithopone compared with Lithopone converted to very low reactivity and both used in the manu- of flat wall paint is shown in the following table. This Lithopone was 461 M consistency range and the "P-C" factor normally should have been be- 5.5 and 5.0.

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Table III

Lithopone Flat Wall Paint Consistencies*

ctor	1 Day	2 Days	4 Days	7 Days	30 Days
	1970 sec.	3490 sec.	Too thick	Too thick	Too thick
	23 "	25 "	30 sec.	34 sec.	32 sec.

rmer viscosimeter, seconds for 50 revolutions with 350 grams.

In obtaining high initial consistencies of products such as painter of the so-called "one-coat" type, use may be made of Lithopones of a high ctor. If used with a poor wetting vehicle containing a large percentage olymers, this abnormal consistency can be maintained on storage in the considerable periods of time, thus overcoming one of the difficulties ly encountered in this type of enamel production, viz., the "sliding off" nsistency within a few weeks of the date of manufacture.

A Lithopone having an "A" factor of 26-H seconds, a "B" factor of a "P-C" factor of 9.1, mixed and ground in a highly polymerized Sardine ter vehicle, and thinned with a China wood oil-Perilla-Ester vehicle in China wood oil has been brought close to the threshold of gelation, an enamel of abnormally full consistency, which held in the can. If the allowed to stand over night a further marked increase in consistency If the grinding temperature was raised from 125° F. to 154° F. the owed an increase in body from 475 seconds (Stormer) to 1070 seconds. other similar experiments showed that grinding temperature played an role.

It is believed that with a vehicle of the above characteristics, active polar constituents are able to attach their molecules so firmly rface of the Lithopone particle that they are not dislodged on storage

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can. They thus maintain intact both the primary and secondary envelopes the particle which in turn determine the structure of the mass and the ity of the enamel. Increased temperature aids in the setting up of the structure.

mination of the "P-C" or Surface Reactivity Factor

The following procedure developed by C. D. Downs is considered an rimate measure of the surface reactivity of lithopone pigments.

Definitions: The weight in grams of pure linseed fatty acids required to effect inversion of 100 grams of a pigment suspended in a non-polar liquid (mineral spirits or naphtha) is taken as the Absorption Inversion Factor, or "P-C" factor of that pigment.

Pure linseed fatty acid is defined as the product obtained by the distillation of a sulphuric acid treated linseed oil, and having an acid value of 200.

Note: Linseed oil fatty acid (2120) as obtained from Wecoline Process Company or Woburn Degreasing Company is specified as: Acid value, 195 minimum; Iodine number, 195 minimum. At 195 acid value it would therefore, for purposes of this test, be considered as 97-1/2% pure. The (2120) should be fresh and very pale in color and produce a solution clear and colorless. It should be stored in full, amber glass containers.

Reagents

Standard Linseed Fatty Acids Solution

(a) Determine very accurately and exactly the acid number of the (2120) used. This should be done frequently to check on any deterioration which may occur. Be sure sample is representative.

(b) Weigh accurately into 500 c.c. volumetric flask (2120) equal to:

$$\frac{10 \text{ grams} \times 200}{\text{Acid No. of (2120)}}$$

Use capped weighing pipette. Avoid losses during transferring. Keep (2120) homogeneous while weighing.

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(c) Make up with clean, water-free (348) to exactly 500 cc.

Assuming the acid number of Pure Linseed Fatty Acids to be 200, this solution contains exactly 0.02 grams/cc. of Pure Linseed Fatty Acid.

If the weight of the fatty acids is not exact, this is taken into consideration by calculation in establishing the value of the solution. For example, assume the acid value to be 198. The amount of fatty acids for 500 cc. of solution would be:

$$\frac{10 \text{ grams} \times 200}{198} \text{ or } 10.101 \text{ grams}$$

If the weight actually added however was 10.200 grams, the value of the solution must be calculated by determining fatty acid per cc. (dividing by 500) to give 0.0204 grams and multiplying by the factor representing the relationship of the acid value to 200. In this case $\frac{198}{200} \times .0204$ to give the value of 1 cc. of the solution as 0.0202 grams pure linseed fatty acids.

Procedure: 10 grams of pigment is accurately weighed and transferred to a glass slab. Five cc. of (348) - mineral spirits is then added to the pigment and worked in with a spatula. The linseed fatty acid solution is then added drop by drop from a burette, working in well and mixing all thoroughly with the spatula after each addition. After the addition of the first few drops a heavy, short or flocculent and thixotropic paste will result.

As continued additions of the fatty acid are made the paste gradually loses its flocculent character and the end point, disappearance of thixotropy, is sharp.

cc. linseed fatty acid solution taken, multiplied by 100, multiplied by the value of 1 cc. in terms of pure linseed fatty acids is the Adsorption Capacity Factor of the pigment used.

Strength of Linseed Fatty Acid Solution

The solution deteriorates and breaks out on aging, consequently [illegible] be used when fresh and not used when more than a day old. Great care [illegible] be used in holding this solution at standard value.

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Time Element

In order to stabilize the time element and allow sufficient time for making the mix thoroughly homogeneous after each addition of the fatty solution, each test should consume 25 - 30 minutes normally for lithopone samples.

Endpoint

The endpoint, defined as disappearance of all flocculation, is determined by gathering up all the thoroughly mixed paste into one pile when the endpoint is approached, and drawing the spatula lightly over it to spread it out in a thick layer on the slab. The mix, at the endpoint, should spread absolutely smoothly with no tendency toward unevenness, breaking, or flocculation. The mix should not pile up "slushily" in front of the spatula as it is drawn over it should flow smoothly under the spatula. If particles of the mix become dry as it is spread out thinly, and are gathered into the rest of the mix, they should not be confused with the flocculent nature of the wet paste before the endpoint is reached.

Normal pressure is used on the spatula while mixing in order to break up pigment agglomerates and allow thorough and smooth incorporation.

Uniformity of Deliveries Based on "P-C" Factors

It has been pointed out that the "P-C" factor can be controlled by partially neutralizing the surface attraction of the Lithopone particle to any desired point by means of treating agents during manufacture. Hence it is possible to produce successive batches of Lithopone having the "P-C" factor held within narrow ranges. A high consistency Lithopone, therefore, may or may not have a high "P-C" factor.

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Eight successive deliveries of a competitive Lithopone having an ...ctor of 32-H seconds and a "B" factor of 37 gave "P-C" factors within the ...of 4.6 to 5.6. Eight batches of Coffeyville production with an "A" factor ...of 15-H to 19-H seconds gave "P-C" factors of 7.9 to 8.9. Seventy-six ...es in the middle consistency range of 15 to 26 "A" factor came within a ...range of 5.0 to 6.1.

The margin of safety necessary to prevent after-bodying is de...nt on the sensitivity of the vehicle used and the paint formulator must be ...d by his own findings.

It is desirable that the different laboratories familiarize them...es with the details of the test and know that they can check their findings ...those of other laboratories through the use of a standard Lithopone having ...own "P-C" factor.

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