Unfinished Problem

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Detroit, Michigan

From a paper read before the Cin
Indianapolis Paint & Varnish Produ
30, 1934. (Official Digest, Federatio
Varnish Production Clubs, M

PRODUCTS

PIGMENTS, COLORS, CHEMICALS

Product			
	Zinc	*Lead*	
"Ozlo" Leaded Zinc Pigment	60%	40%	
	65%	35%	
"Permolith" Lithopone	Normal	Blued Unblued	All oil absorptions
"Permolith" Lithopone	Reinforced 50-53% Zinc Sulphide Titanated 15% TiO_2		
Pure Zinc Sulphide			
White Lead	Old Dutch Quick Process	Dry Pulped in Linseed Oil	
Colors, Dry & Pulped in Linseed Oil	Chrome Yellows—C. P. and Reduced Chrome Greens—C. P. and Reduced Chinese Blue Para Reds and Toners Toluidine Reds and Toners		
Litharge	Glass Makers Color and Varnish Makers Insecticide Manufacturers Oil Refiners		
Red Lead	70%, 85%, 92%, 95% Pb_3O_4		
Zinc Sulphate ("Rayon" brand)	$ZnSO_4 — 5H_2O$ $ZnSO_4 — 1H_2O$		
Cadmium Metal	99.5+% Pure		

THE OZARK SMELTING & MINING CO.
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OZARK — MILLS — MINES — PIGMENTS — COLORS — CHEMICALS

FOREWOR

THE problems treated in this
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much discussion. Dr. Holley's trea
is based on his wide acquaintance an
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Williams Company and allied co
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proving ground or understanding

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No major change has been ma
ment processes until thoroughly pr
lation, application by practical paint

THE OZARK SMELTIN

UNFINISHED PAINT PROBLEMS

An address by Dr. C. D. Holley, to the Cincinnati-Dayton-Indianapolis Paint and Varnish Production Club, May 30th, 1934.

Those of us who are actively concerned with paint formulation find considerable difficulty in keeping our feet on solid ground. A large number of new raw materials continually demand our attention; new lines of merchandise are required to fit the ever-changing sales picture; frequent discussions must be held with sales departments on current sales problems. All these activities leave us little time to devote to many of our basic paint problems.

Several of these basic problems furnish the ground work for our discussion this evening, and perhaps we can gain the most benefit by conducting a symposium or "round table discussion," taking as our subject "Unfinished Paint Problems."

Granulation

Our first unfinished problem is "Granulation" of mixed paints. The number of paint manufacturers who say they don't have any "Granulation" is rather amazing. They are sincere in their belief, but your speaker has never seen a can of anybody's mixed paint containing zinc oxide, japan drier and a trace of moisture, which would not show an objectionable degree of granulation within a year, providing the paint was kept in a warm place.

Aside from objectionable settling or caking in the package, there is nothing which vexes the user of mixed paint more than to open a can and find it full of granules or "corn flakes," which can be eliminated only by straining at the expense of a considerable wastage of material and loss of time.

A tremendous amount of money has been spent by paint manufacturers to instil confidence as to the desirability of using mixed paint. Unless we do a better job than we have done, we cannot blame the customer if he returns to the use of white lead in oil.

We know what granulation is, viz.: the formation of zinc soaps of limited solubility, which in turn are deposited from a supersaturated solution in the oil, resulting either in small granules throughout the paint, or by slow growth develop into large "corn flakes" on the surface of the paste portion.

We know that in order for granulation to develop in linseed oil paints, there must be present zinc oxide, driers and moisture. These items are present in all white and tinted mixed paints. Therefore, granulation will take place in all such paints if they are allowed to stand for a sufficient length of time.

Our problem is to retard the rate of granulation so as to insure usage of the paint before granulation has progressed to an objectionable degree. This is accomplished by eliminating as far as possible, those agencies which promote it.

Unfortunately, the most active agent we have to contend with is elevated temperatures and this condition is beyond our control. Granulation proceeds about five times as rapidly at 100° F. as at 70° F. Your speaker has examined cans stored for only a year in Florida and southern Texas which had granulated as badly as in five years storage north of the Ohio River.

The use of acid refined oil strongly accelerates granulation. The higher the acid value the more rapid the granulation. On the other hand, alkali refined oils, because of their freedom from oil acids, are very effective in retarding granulation.

The character and quantity of drier used ha
driers are strong incitors of granulation. Lino
and low in manganese and cobalt are among th
mental. Unfortunately the use of linoleate drie
the paint in the can, and sales departments which
ness usually pay the penalty of excessive granu
of light colored rosin driers.

Rather strong claims have been made that t
container through the closure, due to changes in
tric pressure, is a big factor in causing granul
for their basis the well known fact that the zinc
linseed oil are less soluble and, therefore, precip

Our investigations show that while the volu
and the type of friction closure have a distinct
nevertheless if the other important factors whic
present, viz.: elevated temperatures, acid refin
little moisture, and the usual type of lead-fr
excessive granulation will take place in a vacu
sealed container.

Turpentine and turpentine driers have litt
factors are present which promote rapid granul
ceeds quite slowly, turpentine, through its greate
soaps, is of benefit in delaying the appearance of

If the oils and driers exert a marked influe
tion, we would expect that the type of zinc o
produce equally important differences, and this
taining substantial percentages of excessivel
granulate rapidly.

On the other hand, the high leaded zinc
types, because of the intimate association of
same particle, and because of the absence of exc
retarding influence on granulation.

Other conditions being equal, we find that
leaded zinc, the rate of granulation is only one
equivalent mechanical mixture of lead-free z
is used.

The following tables indicate comparative
like conditions with a conventional pigment c
zinc oxide and Titanox.

Effect of Vehicle Composition o

Composition	
Oil	Drier
Refined (AV 2.7)	Rosin Free
Refined (AV 2.7)	Absent
Refined (AV 0.3)	Rosin Free
Refined (AV 2.7)	Rosin Free
Refined (AV 2.7)	Rosin Free*
Refined (AV 3.0)	Rosin
Refined (AV 4.0)	Rosin Free
Refined (AV 4.0)	Rosin
Refined (AV 2.7)	Naphthenic type
Raw (AV 2.9)	Rosin Free
Raw (AV 2.9)	Rosin

* Drier increased 100%.

Leaded Zinc vs. Mechanical Mixtures of White Lead and Zinc Oxide

	Composition		Comparative Rate
Pigment	Oil	Drier	of Granulation
Mechanical Mixture	Raw	Rosin Free	3½
35/65 Leaded Zinc	Raw	Rosin Free	2
Mechanical Mixture	Refined (AV 3.0)	Rosin	7½
35/65 Leaded Zinc	Refined (AV 3.0)	Rosin	3

Therefore, if we are to retard the rate of granulation in our mixed paints to a point where it will not be noticeable even with a slow sales turnover, we should use:

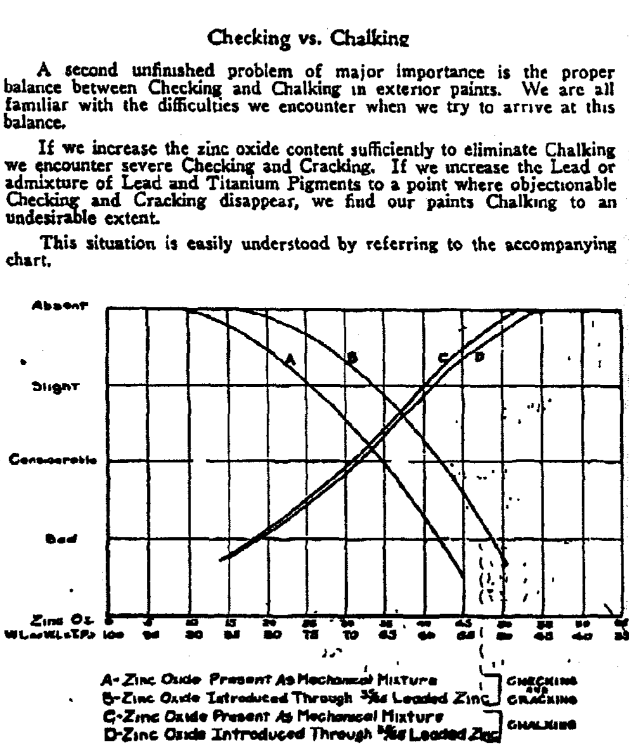
1. An oil having an acid value as close to zero as possible.
2. The minimum amount of rosin-free drier.
3. An approved grade of 35/65 leaded zinc.

Checking vs. Chalking

A second unfinished problem of major importance is the proper balance between Checking and Chalking in exterior paints. We are all familiar with the difficulties we encounter when we try to arrive at this balance.

If we increase the zinc oxide content sufficiently to eliminate Chalking we encounter severe Checking and Cracking. If we increase the Lead or admixture of Lead and Titanium Pigments to a point where objectionable Checking and Cracking disappear, we find our paints Chalking to an undesirable extent.

This situation is easily understood by referring to the accompanying chart.



These graphs represent in a broad way, performance of the different pigment combinat over a three-year exposure period For sim are included with white lead

The curve marked "A" represents the che ance of ordinary zinc oxide with white lead o and titanium pigments. At 25% zinc oxide is "slight," at 35% "considerable," and 42% "b

Curve "C" indicates the chalking tendenc It is "slight" with 40% zinc oxide, "conside about 20%.

At 33% zinc oxide content, we have de with the same paint.

Our problem is, obviously, to reduce tendencies of the zinc oxide, so we can use the region of "slight" chalking with practical

Our own organization has attacked this the high leaded zinc oxides in which the eliminated This type of pigment has a ve checking and cracking compared with mecha composition.

Graphs "B" representing the checking, acteristics of leaded zinc show that zinc oxi increased without encountering checking tro chalking is reduced. With a mechanical mi of ordinary zinc oxide we have slight ch whereas with leaded zinc we may have ne reaching the "slight" checking phase, and t terially lessened, becoming intermediate siderable"

If we can elevate the chalking curve the checking tendencies, we could move position where we could use upwards of 35% 50% of leaded zinc, and have a mild degree very satisfactory from both a durability and

From our exposure studies this proced the use of relatively small percentages of p terially delays the initial chalking and retar first eighteen months of exposure.

High Hiding Power P

On other occasions your speaker has dis with the use of titanium and zinc sulphide pi

Today we find the users of titanium groups. First, those using a moderate per titanium-barium pigment. Second, those centages of 35% to 50%. Third, those usi 10% to 12%—with a moderate percentage of

Because of the many features involved, clearly shown which of these three grouping ever, one feature is very evident. As the pigment, or titanium oxide plus inert pigmen zinc oxide can be introduced into the pain difficult to produce a paint having balanced durability.

Our exposure tests show consistently this situation is through the use of a hig have we found a mechanical mixture of white lead and ordinary zinc oxide, to give as satisfactory durability with the titanium pigments as is obtained when replaced with a similar content of an approved 35/65 leaded zinc.

The use of leaded zinc plus a percentage of heat processed tung oil to retard chalking appears to have solved our major problems in the use of titanium pigments in outside whites. We have, however, a definite and increasing demand for better tint retention of our light colors, and the use of zinc sulphide has been suggested as a means of improving this situation.

Our further experience with pure zinc sulphide as a paint pigment for exterior usage is encouraging. As would be expected, it has behavior characteristics of its own, which must be learned and definitely recognized if we are to formulate with it successfully.

If we avoid the use of acid refined oils and rosin driers, use 35/65 leaded zinc as the source of zinc oxide, and eliminate basic carbonate white lead in favor of basic lead sulphate, we can expect very satisfactory durability and improve our tint retention.

Just why the presence of basic carbonate white lead in zinc sulphide paints should cause early and excessive checking and cracking, and that replacement with basic lead sulphate overcomes this trouble, is difficult to understand. It is, however, evident from our exposure studies, that the limiting factors with zinc sulphide formulations are quite different from those of the titanium pigment paints.

Usage of Soybean Oil

A fourth unfinished problem is the satisfactory use of soybean oil and other oils of the semi-drying type. The domestic soybean industry is one of the young giants in the commercial field which is demanding attention with increasing insistence. The rate of growth has been amazing but is easily understandable when viewed from the effect of tariff enactments.

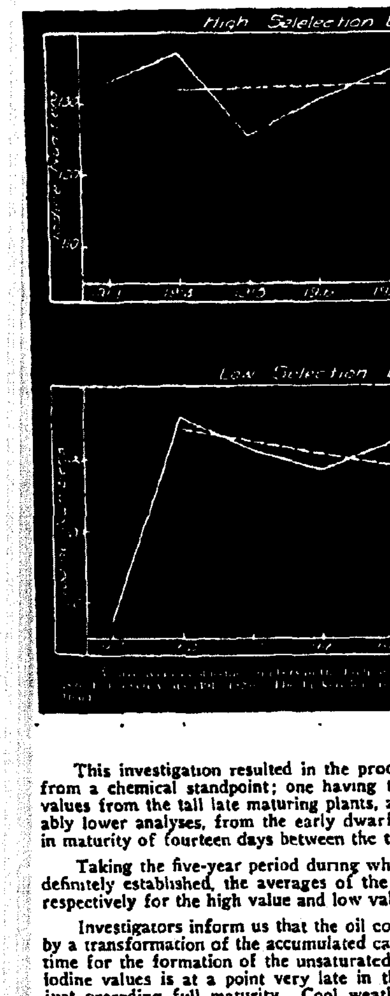
Today there is a very strong economic trend towards a much larger domestic soybean industry with increasing insistence by agricultural interests that a substantial percentage of soybean oil be used in place of linseed oil from imported flax seed in our various paint products. Their argument, which is entirely logical, is—"if we buy your paints you should buy our oil."

If we are to use a substantial percentage of soybean oil in manufacturing our paint products, our natural inclination is to inquire what can be done to improve the drying qualities of this oil.

Assuming that the iodine value is an approximate measure of the drying value, other conditions being equal, an interesting investigation was conducted at the University of Wisconsin, beginning in 1912 and extending over an eight year period in an effort to raise the iodine value by selective breeding.

Starting with the beans from a single plant, the oil of which had an iodine value of 132, a crop was obtained having a high of 133 and low of 108. These were used as the starting points for breeding oils of high and low iodine values. For seven successive years the beans from the plant having the highest iodine value in the high line were selected for planting, and a like treatment followed for the low line.

The results obtained by the University of Wisconsin investigators shown on the following chart indicates first, that improvement in the drying quality of soybean oil is not likely to come through the usual process of selective breeding, and second that climatic variations produce definite effects on the iodine value.



This investigation resulted in the proc
from a chemical standpoint; one having t
values from the tall late maturing plants, a
ably lower analyses, from the early dwarf
in maturity of fourteen days between the t

Taking the five-year period during wh
definitely established, the averages of the
respectively for the high value and low val

Investigators inform us that the oil co
by a transformation of the accumulated ca
time for the formation of the unsaturated
iodine values is at a point very late in th
just preceding full maturity. Cool weath
value as it permits the plant to pass th
formation under conditions which favo
highly unsaturated glycerides.

An increase to an average iodine value of 140 would appreciably improve the drying qualities of soybean oil It may be doubtful, however, if this can be brought about, as it appears that an average of 135 to 136 is about the physiological limit of the soybean plant.

There remains one other possibility. If two soybean varieties could be found having fairly high iodine values but in which the iodine value is determined by different genetic factors, there is the possibility of isolating a superior type from a hydrid between them. This would involve so much work and so many chemical analyses that soybean investigators have hesitated to undertake this problem.

It appears, however, that there are other factors which can affect the drying of soybean oil besides iodine value. We know that freshly pressed linseed oil contains anti-oxidant substances which slow down the rate of the oil very appreciably. These anti-oxidant bodies or "footy" material are partially removed by aging the oil and the drying rate is thereby considerably improved.

Raw soybean oil also contains a considerable quantity of these anti-oxidant bodies, the proportions of which vary, and they are apparently much more difficult to remove by aging than in linseed oil This explains why different lots of raw soybean oil having similar iodine values are frequently different in their drying qualities when incorporated into paints.

If we are to use maximum quantities of soybean oil in paints it may be necessary to use a partially refined soybean oil, in which the anti-oxidant bodies have been partially removed by a treatment considerably less expensive than the usual alkali refining process.

If in order to obtain paints having the best all around performance, we find it necessary to use a mixture of pigments, it would be logical to expect that the best soybean oil paints would contain a mixture of oils This appears to be the case, and we have found that a mixture of 8 parts linseed oil, 4 parts soybean oil and 1 part processed tung oil, dries about as well as linseed alone. Doubtless other equally satisfactory oil mixtures are in current use

Our exposure studies with soybean oil paints reveal some interesting features. We find that at least a week of excellent drying weather should intervene between coats, if we are to prevent early checking and cracking of the top coats, due to their greater rate of contraction or shrinkage through more rapid oxidation.

This tendency to check and crack is materially reduced if a refined soybean oil is used, i. e.—one in which the "break" containing the anti-oxidant bodies has been definitely removed.

Paints containing up to 25% soybean oil (vehicle basis) which has its drying qualities properly balanced by a mixed oil combination, when used with leaded zinc, white lead and titanium pigment mixtures, dries similarly to a straight linseed oil paint and, as far as we can determine, with equal durability.

Because of the tremendous variations in the drying of different deliveries of raw soybean oils—which appears to be largely eliminated if partially refined—it would seem that if soybean oil is to be used on a large scale by the paint industry, the oil producers will have partially to refine their oil to remove anti-oxidant bodies and sell the resulting oil at nearly the raw oil price.

Another interesting development is safflower oil. Nearly every paint manufacturer in the country has received letters promoting this new crop,

and if the farm organizations get back of this
the production of a considerable gallonage of

It will be well worth our while to keep in
stations of the northwest which are doing
safflower. Actually about 300 acres were see
sufficient seed available to plant 2000 acres this

The success of this movement depends
First—acceptance by the stock and dairy inter
concentrated feeding material, comparable to co
and second—adequate tariff protection, particu
already a large grower of safflower

Safflower oil having an iodine value of 14
very fair drying qualities, *if 10% of processe*
exposure tests are not sufficiently advanced t
However, our experience with soybean oil pa
indicate that the slower drying oils give dist
leaded zinc than with ordinary zinc oxide in

Lithopone Paints

Our final "Unfinished Problem" for discuss
paint This is a familiar subject to most of
very brief The particular point we wish to
considerable portion of the consuming public
price for a paint of great durability, there is
of the public who are today very economical
purchasing paint

We as paint manufacturers haven't done
in meeting this situation We have the sem
discussed, available at very economical pri
lithopone, a pigment of great hiding powe
Through the use of these economical raw ma
meet this demand for an economically priced

The large lithopone manufacturers inclu
done a most excellent job in perfecting th
exposure studies of these companies have al
improvments in lithopone paint formulation
next few years continues at the present ra
ashamed of the quality of our lithopone pain
field

The situation becomes much more simp
requirements for repaint work are differen
Very good results are now obtainable on rep
value of a special priming coat, particularly
has been demonstrated by Dr. Browne of the
These priming coats appear to be especiall
lithopone paints.

To date our best results have been obta
of a 40/60 leaded zinc, and 15% inert pigm
avoid the use of acid refined oils and rosi
moderate percentage of semi-drying oil, if
centage of tung oil, has not been found to a
if adequate drying time is allowed between co