Unfinished Paint Problems

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PRODUCTS

PIGMENTS, COLORS, CHEMICALS

"Ozlo" Leaded Zinc Pigment	*Zinc* — *Lead*: 60% — 40%; 65% — 35%
"Permolith" Lithopone	Normal: Blued, Unblued — All oil absorptions
"Permolith" Lithopone	Reinforced 50-53% Zinc Sulphide; Titanated 15% Tio₂
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

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FOREWORD

THE problems treated in this paper are not new to the paint industry, in fact have been the subject of much discussion. Dr. Holley's treatment of the problem is based on his wide acquaintance and experience throughout the paint and raw material industries, and the combined experience of the laboratories of The Sherwin-Williams Company and allied companies approaching these problems from independent angles. There is probably no other chemist in the country who has a better proving ground or understanding of the merchandising and application problems involved.

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Dr. Holley has also acted as a consultant for the Ozark Smelting & Mining Division of this company for many years, and the improvements made in Ozlo Leaded Zinc Oxide and Lithopone have been guided by his practical experience and paint knowledge.

No major change has been made in any of our pigment processes until thoroughly proven in actual formulation, application by practical painters and exposure.

THE OZARK SMELTING & MINING CO.

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 has a marked effect. Rosin driers are strong incitors of granulation. Linoleate driers high in lead and low in manganese and cobalt are among those which are least detrimental. Unfortunately the use of linoleate driers affects the whiteness of the paint in the can, and sales departments which insist on extreme whiteness usually pay the penalty of excessive granulation because of the use of light colored rosin driers.

Rather strong claims have been made that the seepage of air into the container through the closure, due to changes in temperature and barometric pressure, is a big factor in causing granulation. These claims have for their basis the well known fact that the zinc soaps of partially oxidized linseed oil are less soluble and, therefore, precipitate more quickly.

Our investigations show that while the volume of air in the container and the type of friction closure have a distinct influence on granulation, nevertheless if the other important factors which promote granulation are present, viz.: elevated temperatures, acid refined oils, rosin driers and a little moisture, and the usual type of lead-free zinc oxide, rapid and excessive granulation will take place in a vacuum filled and hermetically sealed container.

Turpentine and turpentine driers have little beneficial effect if the factors are present which promote rapid granulation. If granulation proceeds quite slowly, turpentine, through its greater solvency toward the zinc soaps, is of benefit in delaying the appearance of objectionable granulation.

If the oils and driers exert a marked influence on the rate of granulation, we would expect that the type of zinc oxide pigment used would produce equally important differences, and this is true. Zinc oxides containing substantial percentages of excessively fine particles tend to granulate rapidly.

On the other hand, the high leaded zinc oxides, such as the 35/65 types, because of the intimate association of the lead and zinc in the same particle, and because of the absence of excessive fines, exert a strong retarding influence on granulation.

Other conditions being equal, we find that with the "Ozlo" brand of leaded zinc, the rate of granulation is only one-half as rapid as when an equivalent mechanical mixture of lead-free zinc oxide and white lead is used.

The following tables indicate comparative rates of granulation under like conditions with a conventional pigment combination of white lead, zinc oxide and Titanox.

Effect of Vehicle Composition on Granulation

Composition Oil	Drier	Water	Comparative Rate of Granulation
Refined (AV 2.7)	Rosin Free	Absent	1
Refined (AV 2.7)	Absent	1%	3
Refined (AV 0.3)	Rosin Free	1%	1½
Refined (AV 2.7)	Rosin Free	1%	3
Refined (AV 2.7)	Rosin Free*	1%	4½
Refined (AV 3.0)	Rosin	1%	7
Refined (AV 4.0)	Rosin Free	1%	5
Refined (AV 4.0)	Rosin	1%	8
Refined (AV 2.7)	Naphthenic type	1%	4
Raw (AV 2.9)	Rosin Free	1%	2½
Raw (AV 2.9)	Rosin	1%	5

* Drier increased 100%.

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

Pigment	Composition Oil	Drier	Comparative Rate 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:

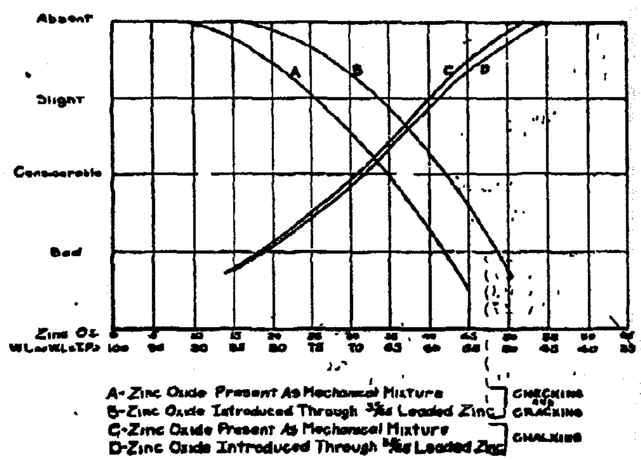
1. An oil having an acid value as close to zero as possible.
2. The minimum amount of rosin-free drier.
3. An approved grade of 35/65 leaded zinc.

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, the checking and chalking performance of the different pigment combinations indicated and evaluated over a three-year exposure period For simplicity the titanium pigments are included with white lead

The curve marked "A" represents the checking and cracking performance of ordinary zinc oxide with white lead or combinations of white lead and titanium pigments. At 25% zinc oxide content the checking effect is "slight," at 35% "considerable," and 42% "bad."

Curve "C" indicates the chalking tendencies of these same pigments. It is "slight" with 40% zinc oxide, "considerable" at 30%, and "bad" at about 20%.

At 33% zinc oxide content, we have definite checking and chalking with the same paint.

Our problem is, obviously, to reduce the checking and cracking tendencies of the zinc oxide, so we can use more of it, and move over in the region of "slight" chalking with practical absence of checking.

Our own organization has attacked this problem through the use of the high leaded zinc oxides in which the excessive "fines" have been eliminated This type of pigment has a very definite effect in reducing checking and cracking compared with mechanical mixtures of equivalent composition.

Graphs "B" representing the checking, and "D" the chalking characteristics of leaded zinc show that zinc oxide contents can be materially increased without encountering checking troubles and the severity of the chalking is reduced. With a mechanical mixture of white lead with 25% of ordinary zinc oxide we have slight checking and severe chalking, whereas with leaded zinc we may have nearly 35% zinc oxide before reaching the "slight" checking phase, and the chalking condition is materially lessened, becoming intermediate between "slight" and "considerable"

If we can elevate the chalking curve somewhat without increasing the checking tendencies, we could move into a still more satisfactory position where we could use upwards of 35% zinc oxide equivalent to about 50% of leaded zinc, and have a mild degree of chalking which would be very satisfactory from both a durability and a refinishing standpoint.

From our exposure studies this procedure appears possible, through the use of relatively small percentages of processed tung oil, which materially delays the initial chalking and retards its development during the first eighteen months of exposure.

High Hiding Power Pigments

On other occasions your speaker has discussed the problems connected with the use of titanium and zinc sulphide pigments.

Today we find the users of titanium pigments divided into three groups. First, those using a moderate percentage—20% to 25%—of the titanium-barium pigment. Second, those using the much higher percentages of 35% to 50%. Third, those using pure titanium oxide—about 10% to 12%—with a moderate percentage of added inert pigments.

Because of the many features involved, our exposure studies have not clearly shown which of these three groupings is the most desirable. However, one feature is very evident. As the percentage of titanium-barium pigment, or titanium oxide plus inert pigment increases, less white lead and zinc oxide can be introduced into the paint, and it becomes increasingly difficult to produce a paint having balanced performance and satisfactory durability.

Our exposure tests show consistently that the best way of meeting this situation is through the use of a high leaded zinc. In no instance 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.

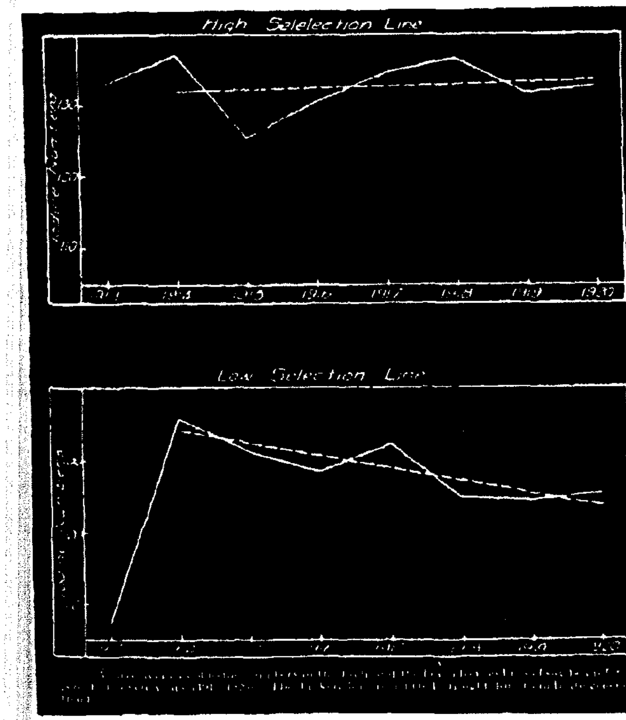
Today there is a very strong economic trend towards a much larger domestic soybean industry with increasing insistence by agricultural interests that a substantial percentage of soybean oil be used in place of linseed oil from imported flax seed in our various paint products. Their argument, which is 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 production of two groups of plants from a chemical standpoint; one having the higher analyses as to iodine values from the tall late maturing plants, and the other, with the considerably lower analyses, from the early dwarf plants, there being a difference in maturity of fourteen days between the two groups.

Taking the five-year period during which the two types of plants were definitely established, the averages of the iodine values were 134 and 127 respectively for the high value and low value groups.

Investigators inform us that the oil content of the soybean is produced by a transformation of the accumulated carbohydrates, and that the critical time for the formation of the unsaturated glycerides producing the higher iodine values is at a point very late in the life history of the plant and just preceding full maturity. Cool weather favors an increase in iodine value as it permits the plant to pass through the critical phase of oil formation under conditions which favor the production of the more highly unsaturated glycerides.

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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 movement it may result in the production of a considerable gallonage of a very useful oil.

It will be well worth our while to keep in touch with the experiment stations of the northwest which are doing development work on the safflower. Actually about 300 acres were seeded last year, and there is sufficient seed available to plant 2000 acres this spring.

The success of this movement depends essentially on two factors. First—acceptance by the stock and dairy interests of safflower meal as a concentrated feeding material, comparable to cottonseed and soybean meals, and second—adequate tariff protection, particularly with regard to Russia, already a large grower of safflower.

Safflower oil having an iodine value of 145 to 150 produces paints of very fair drying qualities, if 10% of processed tung oil be present. Our exposure tests are not sufficiently advanced to draw specific conclusions. However, our experience with soybean oil paints and safflower oil paints indicate that the slower drying oils give distinctly better durability with leaded zinc than with ordinary zinc oxide in typical formulations.

Lithopone Paints

Our final "Unfinished Problem" for discussion this evening is lithopone paint. This is a familiar subject to most of us and your speaker will be very brief. The particular point we wish to make is,—that while a very considerable portion of the consuming public will continue to pay a good price for a paint of great durability, there is another substantial portion of the public who are today very economically minded when it comes to purchasing paint.

We as paint manufacturers haven't done as good a job as we should in meeting this situation. We have the semi-drying oils which we have discussed, available at very economical prices. We have the modern lithopone, a pigment of great hiding power, available at a low cost. Through the use of these economical raw materials we should be able to meet this demand for an economically priced paint of fair durability.

The large lithopone manufacturers including Sherwin-Williams, have done a most excellent job in perfecting the lithopone pigments. The exposure studies of these companies have already taught us much as to improvments in lithopone paint formulation. If our progress during the next few years continues at the present rapid pace, we should not be ashamed of the quality of our lithopone paints in this economically priced field.

The situation becomes much more simple, if we recognize that the requirements for repaint work are different from those of new work. Very good results are now obtainable on repaint jobs. On new work the value of a special priming coat, particularly for white and yellow pine, has been demonstrated by Dr. Browne of the Forest Products Laboratory. These *priming coats* appear to be especially suitable for use under the lithopone paints.

To date our best results have been obtained with 35% lithopone, 50% of a 40/60 leaded zinc, and 15% inert pigment—care being exercised to avoid the use of acid refined oils and rosin driers. The presence of a moderate percentage of semi-drying oil, if associated with a small percentage of tung oil, has not been found to affect the durability adversely if adequate drying time is allowed between coats.

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