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CHROMATE PIGMENT EVALUATION

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Abstract:

A cooperative government industry committee has evaluated nine chromate pigments in three different vehicles in primers for steel, aluminum and magnesium. An important aspect of this investigation was the control of CPVC by adjusting the proportions of a micronized and a fibrous magnesium silicate. This allowed the establishment of a constant PVC/CPVC ratio at a constant PVC. Primers formulated in this way to give equivalent permeabilities showed little if any differences in performance due to variation in the type of chromate pigment.

There are a number of metallic chromate pigments now being used or considered for use in corrosion inhibitive metal primers. In 1950 the Engineer Corps instituted a project to determine which of these pigments was the most effective in primers for the protection of steel, aluminum or magnesium. The Engineer Corps, as represented by R. W. Hill of the Protective Coatings Section of the Engineer Research and Development Laboratories at Fort Belvoir, Virginia, enlisted the aid of an industrial committee to guide them in this work. The Paint Research Department has participated actively in this committee over the past five years. This is a report on the work done by and through this committee.

The committee agreed in the original meeting to a basic plan that was followed precisely throughout the project. Nine chromate pigments were selected for evaluation. These were:

Regular zinc chromate
Zinc tetroxy chromate
Normal lead chromate
Basic lead chromate
Barium-potassium chromate
Strontium chromate
Calcium chromate
Barium chromate
Salt free zinc chromate

These nine chromate pigments were to be evaluated in three vehicles, oleoresinous, alkyd, and phenolic; over three metals, steel, aluminum, and magnesium; under three different conditions, water immersion, salt fog, and exterior exposures.

It also was decided to use a pigmentation consisting of 40% of the chromate pigment, 15% iron oxide and 45% inert, all by weight, in each of the three vehicles. However, beyond this general formulation there was considerable disagreement on the details. It is in the working out of these details that the more pertinent part of this report lies. In particular, the interest is in the method of substituting one chromate pigment for another while attempting to keep all other factors of the formulations constant.

Quite often new pigments are evaluated by merely substituting them at a constant weight in an established formula. Such a method may be satisfactory when comparing two pigments of the same composition, differing only in their method of preparation. Even here there is a danger of radical differences in particle size and consequent radical differences in performance. Obviously, these are not due to differences in the inherent inhibiting qualities of the pigment itself. In the case where the nine different chromates are compared there is an even more obvious objection. For example, in equal weights of lead chromate and calcium chromate there is much more chromate content in the calcium chromate type. This is evident if one considers the higher percentage of lead in lead chromate compared with the percentage of calcium in calcium chromate.

Two other possible approaches would be through a substitution on an equal chromate or an equal available chromate basis. Again, any comparisons between lead chromate and calcium chromate are confounded by the disparities in weight and solubilities of lead and calcium. Simple substitutions on an equal volume basis, although better than a weight or chromate content basis, also may lead to erroneous results through effects on the critical pigment volume concentration. Substitution on an equal cost basis may be of some practical interest but has no place in a research project.

Consideration of the foregoing leads to the conclusion that the following factors should all be controlled in such a project:

1. The chromate pigment content, preferably on a volume basis.

2. The total pigment content again on a volume basis.

3. The composition of the pigmentation other than the chromate.

4. The ratio of the pigment volume to the critical pigment volume. (Control of this factor should also control film permeability.)

The difficulty lies in attempting to control the fourth factor, the ratio of the PVC/CPVC, which in effect amounts to maintaining a constant CPVC. This was done by manipulation of the inerts.

The CPVC of a paint is determined by the vehicle binder absorption of the pigmentation and the way in which that pigment packs in a dried film. The packing of the pigmentation in turn depends upon the size and shape of pigment particles or agglomerates. Magnesium silicates are available with considerably different particle size and shape, such as the fibrous talc, Fibrene C-400, and the micronized talc, #549 Microne Talc. It was considered possible that the use of each of these inerts separately with each chromate pigment might lead to formulations that would all bracket a common CPVC. Then, by blending the two inerts in the proper proportion in a formulation for each chromate pigment, it should be possible to arrive at a common CPVC for all of the formulations within one vehicle type.

It was determined that such a result could be obtained. Thus, nine formulations varying only in type of magnesium silicate were developed for the oleoresinous vehicle with a CPVC of 37.5%. Similar series of paints were developed for the alkyd and phenolic vehicles at CPVC's of 36.5%. If the fact that fibrous and micronized talcs will show only minor, if any, differences in performance in metal primers of equal permeabilities is accepted, the original goal of a series of nine paints differing only in type of chromate pigment has been accomplished.

A sidelight of this investigation may be of interest at this point. It appears that the shape of pigment particles is more influential in affecting the CPVC than is the size. It was found in a specific case that substituting fibrous talc for micronized talc raised the CPVC from 34.2 to 37.0, an increase of 8.4%. On the other hand, with a similar formulation, the substitution of ASP 400 clay for ASP 100 clay raised the CPVC from 45.6 to 47.8, an increase of 4.9%. It is reported that the average particle size of fibrous talc is 8 microns compared with 4 microns for micronized talc. The average particle size of ASP 400 is reported to be 4.2 microns and the ASP 100 to be 0.55 microns. Thus a 2:1 ratio in particle size has had a greater effect on CPVC than an 8:1 ratio. The only apparent explanation is in the particle shape -- the talcs differ significantly between themselves while the clays are similar to each other in particle shape.

The only problem remaining was the establishment of the PVC/CPVC ratio. This was done by setting the PVC at a point 5% of the CPVC below the CPVC or a PVC/CPVC ratio of 0.95. This was done somewhat artibrarily. The attempt was to establish a ratio as close to one as possible without there being a danger that the PVC exceed the CPVC. It is estimated that CPVC can be determined within ± 2%. The experimental error in preparing laboratory batches of paint can be held to ± .10 pounds in weight per gallon, which in these paints is less than 0.5% in PVC or less than 1.5% of the CPVC. Even if these errors are additive there is a margin of safety of 1.5%. Admittedly this is rather thin ground since the CPVC actually does not mark an abrupt change. However, the results indicate that it was a sufficient margin of safety.

When it came to designing the exposure series it was decided for a variety of reasons that a number (actually about 70) of control or check paints should be included. One group of 27 paints utilized the alkyd vehicle, three levels of chromate pigment (15, 35 and 65% at the expense of the iron oxide), with all substitutions on an equal weight basis. The CPVC of each paint was determined and the PVC adjusted to 5% of the CPVC below the CPVC. There also were several specification primers, both chromate pigment primers and standard primers based on other types of pigmentation, such as red lead or zinc dust-zinc oxide. In addition, each committee member was allowed to submit three proprietary systems if he wished.

These paints were then applied by an experienced spray man at a film thickness of 1.5 ± 0.15 mils to degreased cold rolled steel, phosphoric acid cleaned aluminum, and Dow #7 treated FS-1 magnesium. A topcoat of the specification paint 3-173 was applied over half of the surface of those panels destined for exterior exposure. The panels were edged and exposed in triplicate. The water immersion tests were run in the Cincinnati water works in running water at uncontrolled temperatures (generally between 40 and 50° F). The salt spray tests were run in Parker Rust Proof's 20% salt fog room. The exterior tests were run at National Lead's Long Island site.

We will concentrate on the results of the exterior tests on steel substrates which are of the most interest. They were graded last after 30 months exposure. At this time one each of the triplicate panels was stripped and examined for underfilm corrosion. The remarks here are based on this observation.

A cursory examination of the entire set reveals immediately that the "Evaluation" primers show the most consistently good performance. This is the group in which all factors but the type of pigment was controlled. As a group and individually they are better than the specification primers and in many cases they are better than the proprietary primers. The "Check" paints as a set were more erratic and generally poorer. This is surprising in that the PVC/CPVC ratio was controlled although the CPVC was not. It is believed that a part of this may be due to deficiencies in technique, both in the formulation and in the preparation of these primers.

The interesting point here is that excellent primers have been formulated strictly on a theoretical basis in three different vehicles. The main basis for this theoretical work was the CPVC concept. It behooves us to give strong consideration to this concept not only in formulating new primers but also in evaluating new pigments. The method used here to control the CPVC should be applicable to almost any primer and should be very useful.

Actually there is little basis for selecting any one chromate pigment as being outstanding for the inhibition of the corrosion of steel. It would seem that this method of comparing pigments tends to equalize their performance. Such a result is not too surprising since it is quite possible that the metal ion from the pigment has no influence on the inhibition given by the chromate ion in that even the most insoluble chromate is capable of furnishing more than the required amount of chromate to impart inhibition. This is a valuable conclusion since it allows the selection of chromate pigment on the basis of availability and/or cost rather than performance.

A complete report on this work prepared by the Engineer Corps is scheduled to be published. A preliminary copy of this report has been reviewed. The conclusions arrived at are in direct contradiction to the conclusions stated here. It is felt that the main reason for this difference in opinion is in the use of a rather peculiar scale for rating corrosion. This consists of two ratings which are averaged to arrive at the final rating. These are as follows:

Distribution		Degree	
None	10	None	10
Few Spots	9	Trace	9
Scattered	8	Very Slight	8
Generally Scattered	7	Slight	7
General	6	Slight to Moderate	6
Concentrated	5	Moderate	5
Continuous	4	Severe (Pitting)	4

It would seem that in this scale too much emphasis (10 down to 6) is paid to differentiating between degrees of corrosion that well could arise from experimental error. Too little emphasis (6 down to 4) is paid to degrees of corrosion that probably are significant. Thus in the "Evaluation" set of primers no rating was shown of less than 6 for corrosion, and yet an attempt has been made to rank all of the chromate pigments in their order of performance.

An effort has been made to reconcile the divergent views of these results prior to publication.

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