RECEIVED
MAY 3 1955
THE SHERWIN WILLIAMS LAB.

May 24, 1955
10:00 AM

- - - - - - - - - - - -

G. G. Schurr
No. 14

METAL PRIMERS

The Sherwin-Williams Co.

P. V. and L. Annual Symposium

May, 1955

Cleveland, Ohio

Abstract:

Recent work in Paint Research on metal primers covers a diversified set of projects. These include variations in the polyvinyl butyral resin used in wash primers; evaluation of the inhibitive pigments basic lead silico- chromate M-50 and "crude" zinc chromate, D 3082; test methods for oil penetration and corrosion resistance, and a study of degrees of sandblasting.

The purpose of the work done on metal primers in Paint Research is to provide information from which the development laboratories can design new products or improve old ones. This naturally overlaps to some extent the purpose of much of the work in the development laboratories. The primary difference is one of viewpoint. In most instances the development laboratories are aiming at a specific product for a specific end use. Paint Research looks for useful basic information although we may be working on a specific product.

The field of metal primers is so complex that we cannot hope to cover all aspects with the limited number of man-hours that are available. Therefore, we must specialize to some extent. Pigments that have corrosion inhibitive properties have been one of the fields of interest for a number of years. Other components of the pigmentation, particularly inerts, have received attention from time to time. Generally conventional vehicles have not received much attention except for work on wetting action and brushability. Of the higher polymeric synthetic vehicles the most work has been done on vinyl copolymers, polyvinyl butyrals, and epoxy resins. Testing methods, critical pigment volume concentrations, non-pigmentary inhibitors, and even competitive products have been active projects from time to time.

The foregoing gives a broad picture of our activities. We will attempt to clarify the scope of our work by discussing several projects that have been active during the past year.

Zinc Rich Primers

English paint and corrosion periodicals have been filled with advertisements and papers on zinc rich metal primers. These are primers based on very high loadings of zinc dust (93 - 96% by weight) with a polymeric type binder. The theory is that at these high zinc contents electrical contact is obtained from pigment particle to pigment particle. Thus galvanic protection should be available for the protection of steel substrates similar to that obtained from hot dipped or electrolytic zinc coatings. It was claimed that excellent adhesion and film character could be obtained, while on exterior exposure complete protection could be obtained across a 1/4 inch bare area.

We have investigated zinc rich paints using three different types of vehicles; solution type polyvinyl acetate, chlorinated rubber and polystyrene. A somewhat smaller particle size than standard zinc dust was used, New Jersey Zinc's #122. Even with this zinc dust a very rough film was obtained with all of the vehicles at pigment loadings of 95%. However, reasonably good film character was noted, especially after aging. Sanding or other abrasion tended to produce a shiny, metallic appearing surface.

Each of the three polymers had certain advantages. The chlorinated rubber showed the best adhesion and protection to the zinc when not topcoated. The PVAc showed good adhesion and the best resistance to salt spray when topcoated. The polystyrene showed the best suspension properties.

However, all of the primers were disappointing in the protection they imparted against corrosion in salt spray tests. Without topcoats, severe corrosion of the zinc occurred. Even with conventional topcoats such as Metalastic there was considerable corrosion of the zinc pigment. Topcoats such as Carclad or ether ester enamels tended to redissolve the primer vehicles with floating of the zinc dust. The best system was one utilizing a Carclad topcoat with a wash primer sandwich coat.

In spite of the corrosion of the zinc dust in salt spray tests and even in humidity tests, corrosion of the steel substrate also was noted. Little or no protection was offered to scribe marks. Generally speaking conventional primers were superior in all respects. Tentatively, pending results of exterior exposures, we have tabled further work on zinc-rich paints.

Basic Lead Silico-Chromate, M-50

National Lead is attempting to introduce a new type of inhibitive pigment into the metal primer field -- their Basic Lead Silico-Chromate, M-50. M-50 is said to be a pigment made up from a silica core with a shell of basic lead chromate. Presumably it should be as effective as an equal volume of lead chromate at a considerable savings because of its lower cost and lower bulking. To date our tests serve to substantiate this claim, with one notable exception.

M-50 has been evaluated in TT-E-485B as a replacement for the lead chromate, in JAN-P-735 for the zinc chromate, in a vinyl copolymer for lead chromate, as well as in Kromik primer for the zinc chromate and for the zinc chromate and red lead. In all cases in salt spray, humidity, and water immersion tests the M-50 formulation is fully equal to its counterpart control. There is a marked improvement in blister resistance with M-50 when it replaces zinc chromate. Exterior tests so far show little or no differences.

It should be noted that M-50 is not satisfactory with vinyl copolymer vehicles. While basic lead chromate itself exerts a considerable stabilizing action on vinyl resins, M-50 actually accelerates the decomposition. Even an iron oxide such as ferrite yellow gives better performance.

Crude Zinc Chromate

The Dry Color Department has made a so-called "crude" zinc chromate pigment, D3082, which actually is a "leaded" zinc chromate. It is made from a fume obtained from Mineral Products' Coffeyville operations which contains about 12% lead. The lead, even at lower concentrations, causes a discoloration of the product; therefore the term "crude." The predicted cost advantage of this pigment over standard zinc chromate is 4¢ per pound.

D-3082 has been used as a replacement for the zinc chromate in Kromik primer, JAN-P-735, and Fast Dri Primer. In all cases the substitutions were on an equal volume basis. In water immersion and salt spray tests the D-3082 formulations were at least equal to the standard formulations. Two year exterior exposures in Chicago and one year exposures in Florida show essentially no differences in performance. It would seem that this item should be of interest in many primers where color is not critical.

Polyvinyl Butyral Resins

The history of wash primers shows that in this case the egg came before the chicken; i.e. the polyvinyl butyral resin, XYHL, was available prior to the conception of the idea of wash primers. This means that wash primers have been built around this resin rather than the resin being adapted to fit the finish. We have been interested for a long time in the possibilities of improving wash primers either in performance or in package stability by varying the characteristics of the polyvinyl butyral resin. For the past year or more Shawinigan through Monsanto has cooperated with us on this project.

The primary variation of the resin in which we were interested was the polyvinyl alcohol content. Polyvinyl butyral resins are prepared from polyvinyl acetate which is hydrolyzed and reacted with butyraldehyde. This latter reaction can be stopped at any point desired. XYHL contains 18 to 20% hydroxyl groups as polyvinyl alcohol. We obtained a series of resins from Shawinigan ranging from 10 to 30% polyvinyl alcohol content in 5% intervals. These were all based on the same PVAc, so were equal in molecular weight.

Attempts to follow the wash primer reaction by various means such as pH determinations were not too successful. It was hoped that with this series of resins it would be possible to learn enough about this reaction to control it. However, some very interesting results were obtained from performance tests on the wash primers prepared from these resins. The high PVOH containing resins appear to make better wash primers -- particularly for moisture resistance. This is surprising since these resins are more water soluble.

There is a disadvantage with the high PVOH butyral resin. Apparently when sprayed at high humidities it loses the ability to form continuous, tough films with good adhesion. No theoretical explanation of this phenomena is known at the present time. However, it is common knowledge that lead chromate pigmented wash primers show a similar failure. Attempts to eliminate this failure by methods similar to those used to control the blushing of lacquers have not been successful. At the present time we are investigating the effects of various chromate pigments, including chrome phosphate.

Test Methods

It is generally recognized that raw oil vehicles are desirable in structural steel maintenance primers. Their advantage lies in their ability to penetrate through rust and into crevices. However, they also have inherent disadvantages, such as poor durability when weathered, a tendency to pull away from sharp edges, and slow drying. It would be advantageous if durable, thixotropic, faster drying vehicles could be developed that would show better penetration. However, testing by exterior exposure is such a slow process that little progress has been made. A simple quick method of determining the penetration ability of a vehicle or a primer is therefore desirable.

The simplest test, and probably the best, has been to place a few drops (measured) of primer or vehicle on a uniformly rusted surface, observing the wetting action. This method has given good general agreement with known performances but it is not accurate enough for prediction purposes except for gross differences.

Another method that has been investigated is the rate of penetration of a vehicle through a vertical packed column of iron oxide pigment. Here good replication could be attained but the correlation with durability was not good. A third possibility would be simple determinations of surface tension, which we are now trying.

The salt spray test method has long been the subject of severe adverse criticism. While we certainly do not agree with those who claim that salt spray tests are good only for detecting discontinuities in the film, we do feel that there is room for improvement. Recently we have been investigating the usefulness of a dialysis test on a free film. Kittleberger and Elm have reported some results on a test method of this type*. Briefly, a salt solution is placed on one side of an unsupported film and distilled water on the other side. The resistance of the distilled water is measured from time to time. Any drop in resistance is assumed to be due to chloride ions that have penetrated the film. Such a method could be very accurate and reproducible. We do not know the correlation to performance. As yet we are handicapped in our technique of obtaining a free film.

Metal Preparation

The Steel Structures Painting Council has published definitions of "Brush-off," "Commercial," and "White Metal" sandblasting. However, these definitions are quite broad and subject to interpretation. We have prepared specimens according to our interpretation of the SSPC definitions, photographed them for record purposes, painted, and exposed them. Three different types of steel were used for each type of sandblasting, namely:

Intact mill scale HRS
Slightly rusted and wire brushed HRS
Badly rusted and wire brushed HRS

It was noted that in every case the intact mill scale was the easiest surface to clean and gave the best end results.

These original photographs and subsequent photographs of exposed panels should provide a valuable tool for promoting sandblasting and undermining the practice of "ripening" of HRS.

- - - - - - - - - -

The foregoing covers a few of the highlights of our work on metal primers. Obviously this has been aimed at air drying maintenance primers. Work done on Automotive Research and in emulsion paints for metals will be covered elsewhere.

*"Diffusion of Sodium Chloride Through Various Paint Systems," Kittleberger and Elm, Ind. Eng. Chem., 44, 326-9 (1952).