CC: Mr. J. B. Bullitt, Lab.
Mr. J. W. Iliff, Lab.
Mr. C. R. E. Merkle, Lab.
Mr. Stuart Graves, Lab.
Dr. R. B. Davis, Flint

Cross Reference:
National Lead Company
Inhibitive Pigments
Pigments Dept.

Philadelphia Laboratory
July 11, 1949

MEMORANDUM REPORT NO. M-258:

BARIUM CHROMATE PIGMENTS
NATIONAL LEAD COMPANY'S "PIGMENT E"

The National Lead Company is currently promoting a barium and potassium chromate pigment called "Pigment E". "Pigment E" and a barium chromate pigment supplied by the Pigments Department have been evaluated by the laboratory.

"Pigment E" is very slightly better than zinc yellow in a high spot test over rusted structural steel but is not as good as red lead. Exposures over clean steel have not matured yet.

Barium chromate pigment does not show improvement over the red lead controls when rusted auto body steel is the substrate but will be tried against our present zinc yellow controls over rusted structural steel when it can be fitted into a metal protective series.

Sulfate ions have been found present on samples of rust taken from all of our exposure stations. Barium sulfate is insoluble and some work has been done to find pigments (other than red lead) which precipitate sulfate. However, barium chromate is also quite insoluble and removes sulfate ions from solution very slowly. "Pigment E", on the other hand, has so much chromate ion solubility from the potassium chromate that it will release sulfate ions from blanc fixe by mass action. Therefore, it cannot act as a sulfate precipitator.

Details:

A talk on "Pigment E" was given at the April meeting of the Paint and Varnish Production Club by A. J. Eickhoff of the National Lead Company. The talk appears in the April issue of the Official Digest. "Pigment E" is shown to be the double salt $BaK_2(Cr_2O_4)_2$ by X-ray diffraction analysis. However, they report that "Pigment E" when leached successively with water, forms a solution of potassium chromate and leaves a residue of barium chromate. They don't explain how the fact that it is a true double salt is relevant to the subject of metal protection when it breaks down so

readily on contact with water and it depends on this breaking down for the inhibitive action which is claimed. The first washing has been found to contain no barium in our work at the Philadelphia Laboratory although a half-normal solution of chromate is quickly extracted from the pigment or about six times as much as is readily available with zinc yellow. The pigment is not made from the chloride salts but we find it contains considerable soluble chloride.

Data on controls were not shown for exposures, tensile strength, elongation or hardness. A control was shown for salt spray tests on automotive primers but the soluble chromate pigments are at their best in salt spray where osmotic pressure outside the film is great. Data obtained on our Delaware fence are listed in the attached table.

In putting out our exposures on sulfate precipitation, a barium chromate salt was originally scheduled even though it had been tested in the past but was left out when it failed a sulfate precipitation test in which excess barium chromate in a $Fe(SO_4)_3$ solution was shaken and allowed to stand overnight. Before discarding the solution several months later, a test showed that sulfate was no longer present. Barium chromate will not precipitate sulfate as fast as will the stearate, carbonate, nitro-phthalate or lead pigments. Barium chromate will probably prevent the penetration of sulfates through the film but probably does not have quite enough solubility to precipitate sulfates in the rust when added as a pigment. Nevertheless, in view of the recent finding that it will precipitate sulfate although slowly, it should be given a fair try and will be put in the next series. The solubilities of barium chromate and sulfate (blanc fixe, barytes) are 0.00034 and 0.00018 grams per 100 cc respectively.

The presence of chlorides on the barium chromates in the previous work is not known and may have masked the good qualities which we might expect from the pigment as a sulfate precipitator. Chlorides were more than likely present in the iron oxide containing primer. An insufficient amount of chromate in the presence of chlorides is reported (U. Evans, "Metallic Corrosion & Passivity", 1937, P-299) to concentrate the electrolytic attack on small areas forming deep pits. In the presence of excess acids, chromates do not inhibit corrosion and may actually stimulate it by acting as a depolarizer for hydrogen. The pH of zinc yellow is 6.3, "Pigment E" is 6.2 and Barium chromate is 6.8.

On rusted auto body steel, barium chromate is good in raw oil or when supplemented by iron oxide in alkyd but alone in alkyd it fails rapidly. Results of Series 3534 and 3749 are listed in the attached table.

PHILADELPHIA LABORATORY

William C. Johnson

WILLIAM C. JOHNSON

WCJ:ms
ATTACH;

SERIES #3534

Primer	Clean Boilerplate Life in Months	Clean Boilerplate A.S.T.M. 6 yrs.	Rusted Sheet Life in Months	Rusted Sheet A.S.T.M. 6 yrs.
Red Lead in Oil	43	6	40	6
67-718 Red Lead Alkyd	73	9	51	9
67-716 Low Red Lead Alkyd	30	7	13	6
Barium Chromate in Alkyd	72	8	14	6

SERIES #3749

Primer	Life in Months Auto body Steel (Del.)	Clean Boilerplate (Fla.)	Rusty Sheet
Zinc Yellow Raw Oil	50	29	15
" " Alkyd	60+	71	1
67-718 Red Lead Alkyd	60+	66	12
67-716 Low Red Lead Alkyd	60+	71	15
$BaCrO_4$ Raw Oil	55	26	15
" Alkyd	60+	71	1
" /Iron Oxide - Alkyd	60+	66	15
Zinc Yellow/Iron Oxide - Alkyd	60+	71+	15

SERIES #9739

Primer	A.S.T.M. Ratings at 5 Months (Del.) Rusted Channel Iron
Red Lead in Oil	9
67-746 Zinc Yellow Semi Alkyd	5
Pigment E substituted in 67-746	6