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Lead Pigments and Paints*

By ALEX. STEWART†

National Lead Company

Lead pigments have had a wider use in house paints for a longer period of time than any other class of pigments, and yet not too much is known about the chemical composition of the lead pigments we have to work with and, what is more important, very little is known from a technical standpoint about the manner in which lead pigments function chemically in a paint film.

It is not generally known that lead pigments stabilize a film chemically, contribute mechanical strength and toughness, induce flexibility and distensibility, and—important—impart a very high degree of resistance to water sorption. Further, the chemical reactions which take place in a paint film during the course of deterioration by the elements are retarded or stabilized by lead pigments and the rate of the destructive reactions is reduced, resulting in a film of long life and increased durability.

Although lead pigments have been used in single pigment paints for years, the fact that a basic lead pigment is as much a stabilizer in house paints as the stabilizers used in many of our plastics has not been well recognized. Therefore, in this paper I hope to show that lead pigments in house paints should be looked upon as stabilizing agents which combat and neutralize the products resulting from the chemical reactions taking place in house paint films.

Although it is known from a chemical standpoint, many paint technologists may not be aware that the basic lead content of a lead pigment will form substantially water insoluble compounds with the various acidic decomposition products formed in a paint film as it ages. Whether they be formic and propionic acids, decomposition products of the vehicle, or industrial gases such as chlorine, sulfur dioxide and others, lead will react neutralizing them to form substantially water insoluble compounds, resulting in a reduction in the rate of film deterioration.

I should now like to discuss the chemical composition of some of our lead pigments. It will be found that lead is unique among the metals in that it forms a number of pigments which are a well defined series of basic compounds. A basic lead compound or salt may be regarded as a chemical combination of reactive basic lead oxide and a normal lead salt corresponding to the general formula:

$$PbX \cdot nPbO \cdot mH_2O$$

where "n" represents the number of mols of reactive lead oxide combined with one mol of normal salt (PbX) and "m" indicates the mols of combined water. A large number of basic lead compounds have been made by the research staff of the National Lead Company, and the amount of available reactive basic lead oxide varies according to the properties of the acids from which they were prepared.

Table 1 shows a few selected basic lead compounds and it will be noted that with most of the acids listed here, lead will form at least two distinct basic compositions, one more basic than the other. It is important—and of special interest to you—that as the lead pigment in a paint dissociates it will first form the normal lead compound with the breakdown acid, and, finally, a basic compound—before the acid begins to attack more of the original lead pigment. It may be said that basic lead compounds not only neutralize the acids of vehicle decomposition—they form substantially new pigments with the breakdown acids.

The chemical composition of white lead—basic lead carbonate—is of considerable interest. To my knowledge, no one as yet has disclosed the fact that commercial basic carbonate white lead comprises three compounds, two of which are basic and one of which is normal. Before adequate testing equipment was available, some nine different chemical compositions for white lead were reported in chemical literature. *Table* 2 shows the various empirical formulas reported for these compounds.

* Presented at the Friday session, November 17, 1950.
† Director of Research.

Table 1—Composition of Basic Lead Compounds

Acid	Formula of Basic Lead Compound	N	% Basic Lead By Weight
Carbonic	$2PbCO_3 \cdot Pb(OH)_2$	½	28.8
	$4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$	¾	37.7
Sulfuric	$PbSO_4 \cdot PbO$	1	42.4
	$PbSO_4 \cdot 3PbO \cdot H_2O$	3	67.6
Acetic	$3Pb(C_2H_3O_2)_2 \cdot PbO \cdot 3H_2O$	⅓	17.8
	$Pb(C_2H_3O_2)_2 \cdot 2PbO \cdot 4H_2O$	2	52.9
	$Pb(C_2H_3O_2)_2 \cdot 3PbO$	3	67.3
Formic	$Pb(CHCOO)_2 \cdot PbO$	1	42.9
	$Pb(CHCOO)_2 \cdot 3PbO$	3	69.3
Propionic	$Pb(C_2H_5COO)_2 \cdot PbO$	1	38.7
Glycolic	$Pb(HOCH_2COO)_2 \cdot PbO$	1	38.5

Table 2

2 $PbCO_3 \cdot Pb(OH)_2$
3 $PbCO_3 \cdot PbO \cdot Pb(OH)_2$
3 $PbCO_3 \cdot Pb(OH)_2$
4 $PbCO_3 \cdot Pb(OH)_2$
5 $PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$
5 $PbCO_3 \cdot Pb(OH)_2 \cdot PbO$
5 $PbCO_3 \cdot Pb(OH)_2$
6 $PbCO_3 \cdot Pb(OH)_2 \cdot H_2O$
7 $PbCO_3 \cdot PbO \cdot XH_2O$

In the light of present knowledge, acquired through the use of modern scientific equipment, we consider the above compositions to be simply arithmetical mixtures of the following compounds:

Table 3

(1) $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$	Basic
(2) $2PbCO_3 \cdot Pb(OH)_2$	Basic
(3) $PbCO_3$	Normal

The above table shows the progression of the formation of basic carbonate white lead, showing two basic compositions and finally a normal compound.

One method by which the composition of the individual basic lead carbonate may be determined is by studying the changes in electrical conductivity or electromotive force (pH value) of a suspension of lead oxide in a slurry of water and a small amount of acetic acid, as it is slowly treated with carbon dioxide at constant temperature. Any appreciable variation in the pH or electrical conductivity value from a previously established constant value is indicative of the presence of single, insoluble, solid phase, according to Gibbs' Phase Rule.

Figure 1 shows distinctly that there are three consistent pH ranges that exist during carbonation of a lead oxide slurry. The initial slurry has a pH of 9.2 and maintains this pH until the carbon dioxide content of the basic lead carbonate reaches approximately 10 per cent, with about two per cent combined water. The basic lead carbonate produced during this phase of the reaction is represented by the formula:

$$4\ PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$$

At any point before the slurry reaches this 10 per cent carbon dioxide content, it would be a mixture of the basic lead carbonate ($4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$) and free litharge (PbO). It can be seen, in the diagram, that there is an abrupt change to a pH of 6.8, when formation of this compound is complete. As the carbonation is continued at this stage of the reaction, the compound $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$ is changed slowly to the conventional composition of basic lead carbonate, represented by the formula $2PbCO_3 \cdot Pb(OH)_2$. As the carbonation is continued, the pH is reduced until it finally reaches approximately 5.9, at which point normal lead carbonate, $PbCO_3$, is being produced.

Therefore, according to these studies and results, we have only three compounds of lead oxide and carbonic acid, as follows:

$2\ PbCO_3 \cdot Pb(OH)_2$
$4\ PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$
$PbCO_3$—normal lead carbonate

From the above, it is evident—and extremely important—that we have a lead pigment in which the chemical composition may vary as much as 10 per cent in available lead oxide and yet we have a usable pigment for use in house paints.

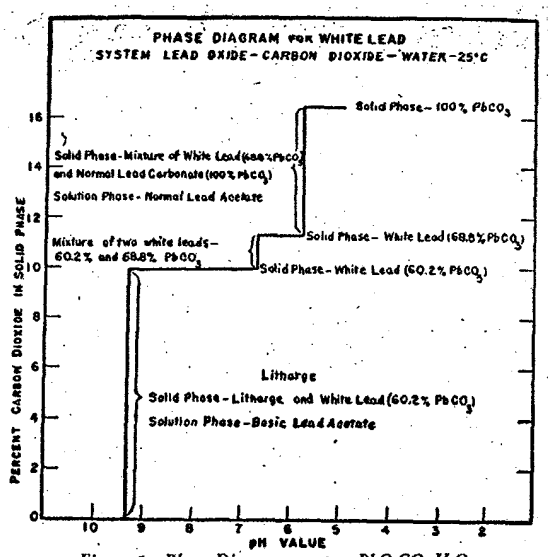


Figure 1—Phase Diagram—system PbO-CO₂-H₂O

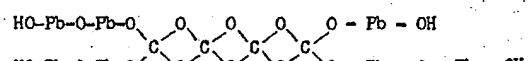
The chemical composition of the lead carbonate formed, according to this technique, are given in the following table:

Table 4—Chemical Compositions of Lead Carbonates

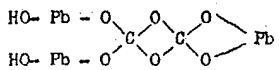
Total Per Cent	*Compound* $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$	$2PbCO_3 \cdot Pb(OH)_2$	$PbCO_3$ (*Normal*)
Lead oxide	88.05	86.33	85.53
Carbon dioxide	9.92	11.33	16.47
Combined water	2.03	2.34	0.00
Available lead oxide	37.73	28.78	.....

The structures of the basic lead carbonates may be represented graphically as follows:

$4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$:-



$2PbCO_3 \cdot Pb(OH)_2$:-



X-ray techniques have been used to establish the presence of definite compounds in our white leads, to corroborate the findings of the pH method. Typical samples of white lead, of the compositions indicated in the pH diagram, were selected for examination with our X-ray spectrometer.

Figure 2 shows the characteristic intensity versus interplanar spacings.

It is evident that the three compounds shown in the pH diagram are substantiated by our X-ray analysis. The existence of these three compounds, as determined by X-ray analysis, is new information that has not been previously reported in the literature.

Figure 3 sets forth the relation of lead oxide, carbon dioxide, and combined water. It is evident from this graph that between 9.9 and 11.3 carbon dioxide, and 2.03 to 2.34 combined water, we are in the range of basic lead carbonate composition. It will also be noted that a carbonate content above 11.3 actually results in dehydration of the basic portion, producing normal lead carbonate.

When the composition of basic carbonate white lead contains an excess of normal lead carbonate, it is similar to a basic lead sulfate which contains an excess of normal lead sulfate—in that its durability in paints is lowered considerably.

LEAD SULFATE

In addition to the basic lead carbonates, the basic lead sulfates are of considerable economic importance. These compounds are present in leaded zinc oxides both as a basic and normal compound.

As prepared by sulfation of lead oxide in aqueous systems, basic lead sulfates correspond to the formulas $PbSO_4 \cdot 3PbO \cdot H_2O$ (tribasic lead sulfate) and $PbSO_4 \cdot PbO$ (monobasic lead sulfate). The compositions of these basic lead sulfates have also been established by pH measurements at constant temperature, as described previously for basic lead carbonates, and have been verified by X-ray diffraction patterns.

Figures 5 and *6* show microphotographs of basic lead sulfate. It can be seen that the basic lead sulfates form two well-defined types of crystals. They differ in this respect from basic lead carbonates which are composed principally of hexagonally shaped crystals.

The hydrous tribasic lead sulfate, as shown (*Figure 5*) is lamellar. The formula is $PbSO_4 \cdot 3Pb \cdot H_2O$.

When the above compound is treated with sulfuric acid there is a transition in crystal form, from lamellar to acicular, as shown in *Figure 6*. This compound is monobasic lead sulfate, $PbSO_4 \cdot PbO$.

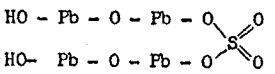
The chemical compositions of the basic lead sulfates are given in *Table 5*.

Table 5—Chemical Composition of Lead Sulfates

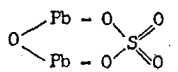
Total, Per Cent	$PbSO_4 \cdot 3PbO \cdot H_2O$	$PbSO_4 \cdot PbO$	$PbSO_4$
Lead oxide (PbO)	90.10	84.79	73.60
Sulfur trioxide (SO_3)	8.08	15.21	26.40
Combined water (H_2O)	1.82	0.00	0.00
Available lead oxide	67.57	42.40	0.00

The structures of the basic lead sulfates may be represented graphically as follows:

Tribasic Lead Sulfate:-



Monobasic Lead Sulfate:-



BASIC SILICATE WHITE LEAD 45X

Basic silicate white lead 45X is a new pigment development. Knowing that only the surface of the individual particle of a reactive pigment is involved in, or affects, the chemical reactions between the pigment and products derived from the vehicle, the National Lead Company research staff designed a pigment particle wherein the reactive compounds are concentrated at the surface. The product is the result of dry phase chemical reactions where, within a given range of temperature, the molecular activity between certain solid acidic and basic compounds is sufficient to cause a chemical reaction in the solid state.

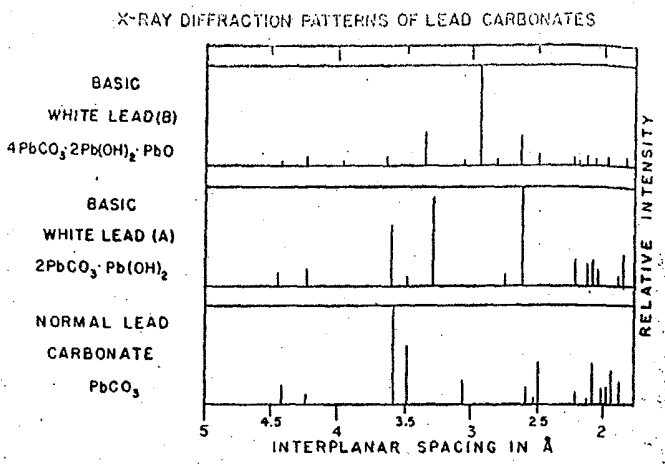


Figure 2—X-ray diffraction patterns of lead carbonates

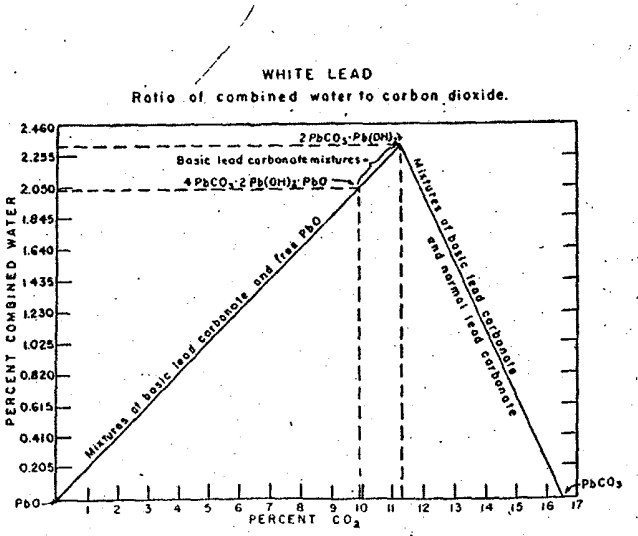


Figure 3—Ratio of combined water to carbon dioxide

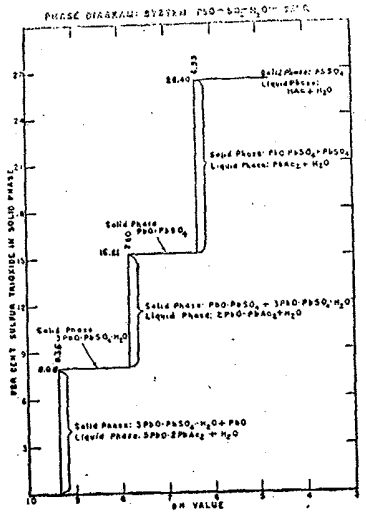


Figure 4—Phase Diagram—system PbO·SO3·H2O

In the preparation of this product, hydrous tribasic lead sulfate, previously described, is reacted with finely ground silica. The result is a pigment comprising a surface layer of basic lead silicate and monobasic lead sulfate firmly bonded to a silica core.

Basic silicate white lead 45X has a specific gravity of 4.0 and a weight per gallon of 33.3 pounds compared to basic carbonate white lead's 56.0 pounds per gallon. The chemical composition of the reactive pigment surface is essentially a double salt of monobasic lead silicate and monobasic lead sulfate.

The following figures provide a clear picture of an inert core of silica with the reactive pigments at the surface.

Figure 8 is a graphical representation of a silica core with its outer layer of reactive pigment.

Departing for a moment from our consideration of pigments, let us give our attention to the vehicle, which is an equally important part of the paint system.

Natural drying oils, bodied and unbodied, are used extensively as the non-volatile portion of the vehicle in exterior house paints. The reasons why these drying oils have retained their prominent place in this class of coating can be better understood when one considers the problems involved in formulating durable exterior paints for wood protection. The requirements of such formulations are as follows: spreading of a heavy film with a minimum number of coats; ease of application over large exterior surfaces; excellent adhesion of the paint film to the wood taking into consideration expansion, contraction and moisture penetration; bright, clean appearance throughout the life of the paint film; and good re-coatability.

In order to obtain these properties, the vehicle portion of the paint should have good pigment wetting, maximum non-volatile content at relatively low viscosity, slow setting for ease of application, controlled penetration, satisfactory dry within 18 hours and finally, should be reasonable in cost and in abundant supply. Vegetable drying oils generally fulfill these requirements. These oils dry by combining with oxygen to form plastic gels through reactions involving oxidation and polymerization. The change over from liquid to solid form consists of three steps: At first there is an induction period during which some volatile material is given off from the film. The second step comprises the rapid absorption of oxygen, accompanied by the transformation of the liquid form into solid state. When the film has

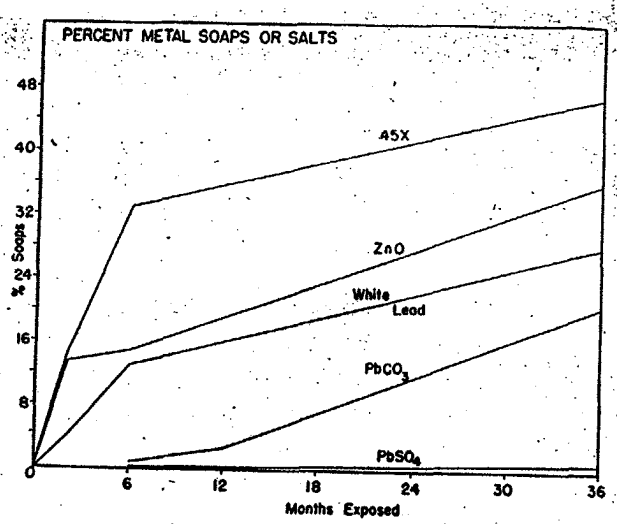


Figure 11

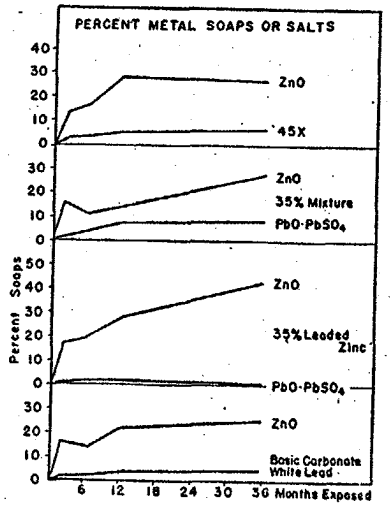


Figure 12—Per Cent Metal Soaps—mixtures of basic lead pigments and zinc oxide

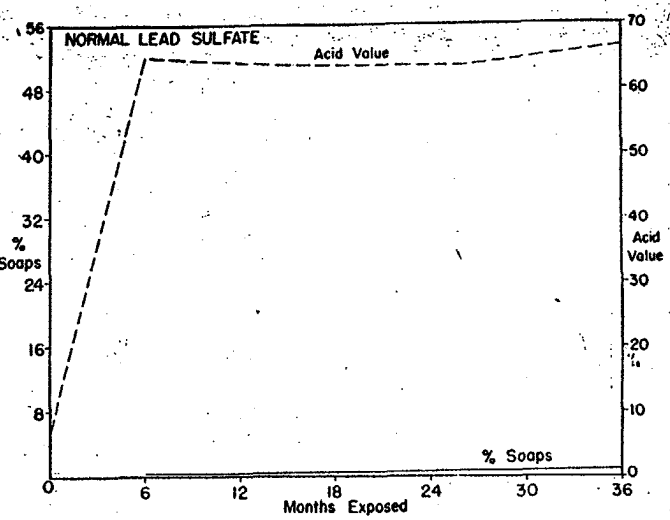


Figure 13—Acid value and per cent metallic soaps for normal lead sulfate

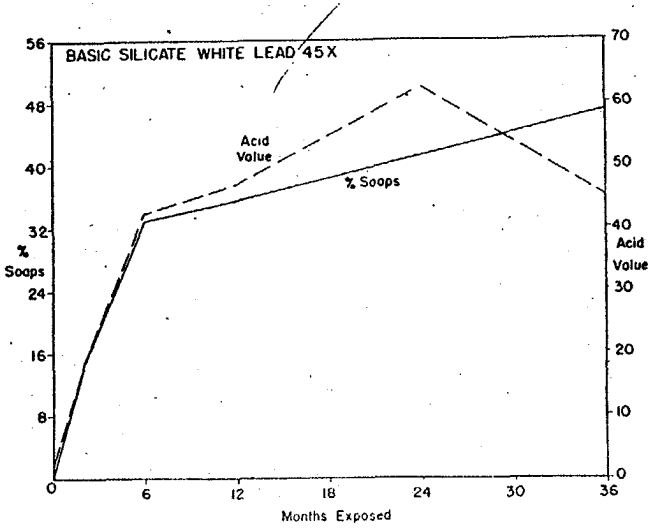


Figure 14—Acid Value and Per Cent Soaps—basic silicate white lead 45x

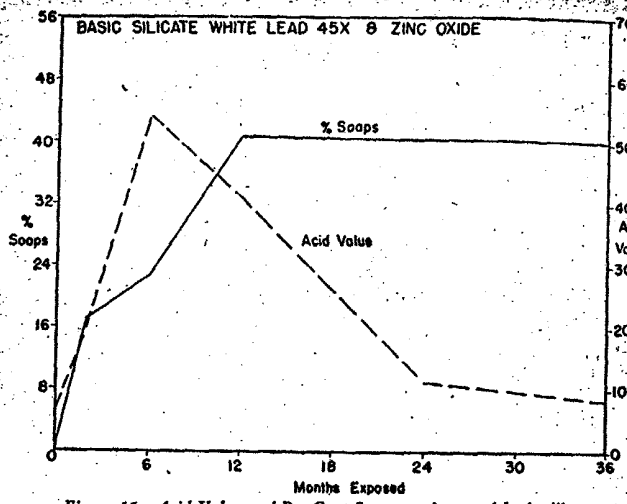


Figure 15—Acid Value and Per Cent Soaps—mixture of basic silicate white lead 45x and zinc oxide

However, when zinc oxide is incorporated into the film, the acid value attains a maximum at approximately six months, then tends to decrease to a relatively low level, as shown in *Figure* 15. This drop in acid number is a characteristic difference which appears to be due to the presence of zinc oxide. This difference in acid value is apparent even though the quantities of soap formed are approximately the same. The rate of soap formation is faster with zinc oxide.

This same effect is also illustrated with a leaded zinc pigment in which the pattern of the acid value follows the same trend as obtained with the zinc oxide-lead pigment mechanical mixtures. This is shown in *Figure* 16.

Excessive zinc oxide in house paint films tends to increase film hardness. Basic lead pigments, however, offset this tendency by imparting a plasticizing and stabilizing effect. It is important to maintain proper balance of the reactive pigments in order to fully realize the best properties of each.

MECHANICAL REINFORCEMENT

Mechanical reinforcement is imparted to films by most pigments.

Variations in particle size and particle shape have a direct influence on the properties of a paint film. White leads of finer particle size seem to impart somewhat better physical properties to films than the coarser white leads. Particle size also affects the physical unit structure apparent in breakdown. In the case of zinc oxide, the coarser particle size pigments impart better film forming properties.

It is also apparent that pigments having a wider variation of particle size allow more compact films to develop. The compact films tend to smaller voids and reduce weak links in the film. The formation of the compact structure with the high solids content helps to reinforce the film.

To reinforce a film, it is important to consider the forces that cause a film to deteriorate. Some of the forces that appear to cause a film to break down are:

(1) Oxidation, resulting in the formation of lower molecular weight organic acids.
(2) Effect of water sorption, water permeability, and water solubility.
(3) Ultra-violet, temperature, and photochemical effects.

As indicated in *Figure* 17, as long as there is a relatively large proportion of reactive pigment present, the tensile strength of the system is fairly pronounced. This is true

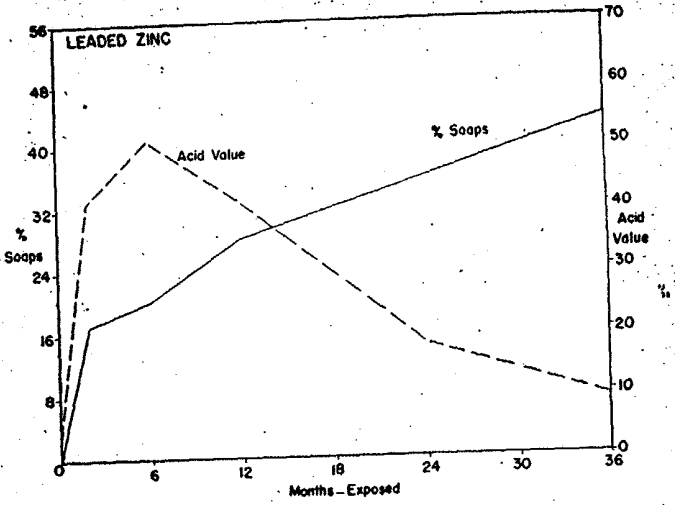


Figure 16—Acid Value and Zinc Soaps—leaded zinc

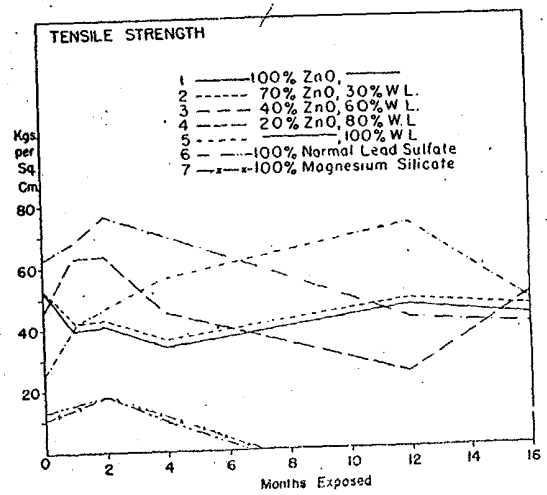


Figure 17—Tensile Strength—mixtures of white lead and zinc oxide