LEAD INDUSTRIES ASSOCIATION
420 LEXINGTON AVENUE
NEW YORK 17, N. Y.

NOT FOR PUBLICATION

LEAD PRODUCTS RESEARCH*

Alex. Stewart, Director of Research

National Lead Company

After an all day session covering the business aspects of the lead industry, any talk on research should be prompt, short, and directly to the point. Moreover, inasmuch as we have more than 5000 years of growing pains behind us the matter of research and development at this time should not seem too important. However, most of our markets began to develop about 50-60 years ago or at about the time organized industrial research began. The necessity of more research in our industry is brought about by the properties of lead and its compounds — since our markets, both actual and potential are a tremendous stimulant to our competitors. Dating back to the time of the alchemists, information of all classes has been provided on lead — therefore, much was known about its properties, and these properties being important, lead becomes a standard for comparison in the chemical and paint industry. A continuous study of improvement of our old products and the development of new lead products becomes a "must".

NEW DEVELOPMENTS

I had a preliminary survey made on new developments during the past few years particularly the last four years and I am sure I have not done too well. Therefore, if I have missed some, or over quote or under quote, it is because I found it very difficult to collect the information.

Metallurgy - A refining process for the removal of zinc by the St. Joseph Lead Co. has been an important contribution to lead metallurgy. This process developed over the past few years for the removal of zinc from lead under vacuum might well set a pattern for the removal of other impurities from lead. It may pave the way for the treatment of lead with hydrous caustic soda employing 2-3 atmospheres of pressure with improved efficiencies in operation. For the removal of small amounts of zinc from lead, this process is very definitely a new development.

Cable Sheathing - This is an important business for the lead industry — in 1948 about 135,000 tons of lead was consumed in this field of business, which is open to considerable competition by materials other than lead. Creep resistance is very important to the life of cable sheathing as the internal pressure of oil or the gas filled cables provide a continuous hydrostatic head which the lead sheath must withstand. Also the daily load power varies, causing

*Presented at the 22nd Annual Meeting Lead Industries Association, April 13-14, 1950, Chicago, Ill., at the Panel Discussion of Lead Consumers.

a daily variance in temperature. Manhole handling to withstand slow bending is another important factor and, last but not least, the weight of lead. All of these factors make lead sheathing a prey for competition. However, there have been a number of developments and as examples I have selected the following. First, the Anaconda Wire and Cable Company have a development in their alloy F-3 indicating what can be had by a study of balancing minor constituents.

Figure 1 shows the resistance to fatigue stresses. The fatigue endurance limit is the unit load that may be applied to a metal 10,000,000 times without failure. According to the information supplied me, F-3 Alloy was able to withstand a load of 1400 psi, while copper lead withstood only 625 psi.

The Hoop stress test is the load that causes a tube to increase in its diameter. A sheath of F-3 alloy withstood a load of 1000 psi and expanded only 1% in one year, while a copper-lead sheath required only 420 psi to expand 1% in one year. This is shown in Figure 2.*

Figure 3* demonstrates the relative life of F-3 alloy. This test consists of deflecting the test specimen one half inch every 70 seconds or 1234 times per 24 hour day. According to these data, F-3 Alloy showed an average life of 30,000 cycles (23-1/3 days), while copper lead showed a relative life of 7500 cycles (6-3/4 days). This is a relative increase in life of over 300% for the F-3 Alloy over the copper-lead alloy.

Kaleo Metal - This is a National Lead Company development of an alloy, highly corrosion resistant for anodes, coils and linings in chromium plating installations and related installations where corrosion due to high oxidizing conditions is a factor. In most electroplating systems the same metal being plated is used as the anode because the rate of plating and the solution of the anode are the same rate. However, in the case of chromium plating, this is not so. If you used a chromium anode, its rate of solution is about 10 times faster than it will plate. Therefore the solution becomes saturated with chromium salts, throwing the whole solution out of balance. Further, a chromium anode is unable to re-oxidize the chromium chromate formed at the cathode to chromic acid. All this means an insoluble anode has to be used and the chromium salts supplied by adding chromic acid to the solution. Lead alloys have been used, such as 6% antimonial lead and 7% tin-lead alloys. However, from a corrosion standpoint these alloys are very erratic in service. In order to obtain any degree of service out of these alloys, it is necessary to form a coating of lead chromate which is relatively insoluble in chromic acid solution. Inasmuch as the lead chromate coating is not too adherent, it falls off, resulting in rapid corrosion. To circumvent this trouble, the recommendation has been to connect periodically the tank lining and coils as an anode in the plating operation for 24 hours. Under this condition a protective coating of lead chromate is built up.

With Kaleo metal none of these precautions are necessary. Moreover, the increased corrosion resistance has been gained at no expense to the desired physical properties.

*Illustrations at end of paper.

Physical properties of Malco Metal

Tensile Strength		Lbs/Sq.In.	Elongation
Malco Metal (Rolled)		4000	55 %
6% Antimonial Lead (Rolled)		4000	47 %

Brinell Hardness		75°F	150°F	210°F
Malco Metal	Cast	10.1	8.6	7.1
	Extruded	8.2	6.1	4.7
	Rolled	7.1	5.2	4.0
6% Antimonial Lead	Cast	11.9	8.7	6.9
	Extruded	11.0	7.6	5.6
	Rolled	7.8	5.6	4.1

Corrosion Resistance of Malco Metal

Chrome Plating Solution

11 Days at 140°F - 250 g. Chromic Acid,

2.5 g. Sulfuric Acid/Liter

	% Loss
	Originally 0.05" Thick
Malco Metal	1%
6% Antimonial Lead	46%

Outside Laboratory Corrosion Test

	Corrosion, inches/year		
	18 hrs.	181 hrs.	397 hrs.
Malco Metal	0.346	0.040	0.017
Tellurium Lead	1.97	Discontinued After 18 hrs.	

Lead Alloy Coatings on Steel Sheet - In the fabrication of air conditioning ducts where moisture, the elements, and temperature provide very highly corrosive conditions, lead alloy coated steel has been found to be very highly resistant. It will be interesting to consider for a moment all the conditions to which these ducts are subjected.

First, moisture. Sulfur as hydrogen sulfide and as sulfur dioxide and sulfur trioxide also carbon dioxide as carbonates. Lead combines with all of these forming insoluble compounds and all of which actually protects the lead from further corrosion.

Pigment Developments - First, I should like to talk about white lead. Although it has been well known for many years, not too many know that a new chemical composition of white lead was discovered within the last twenty years. In 1870 Dr. Strengholm, University of Upsala, Sweden, and in 1892 or 1893 during a lecture in Chicago by J. J. Moreman, both of these gentlemen indicated the possibility of a more basic white lead than the conventional $2PbCO_3Pb(OH)_2$.

It will be seen by referring to the phase diagram in Figure 4 that when the lead carbonate content of the mixture of litharge and lead carbonate reaches the point where there is 60.2% lead carbonate you will note there is definitely a break in the pH value. Upon analysis of the solid phase, the composition was found to be

$$4PbCO_3.2Pb(OH)_2.PbO$$

Continuing the introduction of carbon dioxide until the next break in pH as noted, the lead carbonate content was found to be 68.8% and the analysis of the solid phase at this point showed the composition to conform to

$$2PbCO_3.Pb(OH)_2$$

Continuing the introduction of carbon dioxide beyond this point resulted in the formation of normal lead carbonate

$$PbCO_3$$

Results of this work provided the conclusion that there could be a mixture of two basic compounds of white lead within a range of 60.2 to 68.8% lead carbonate. There is only one other pigment in the chemical world which enjoys the same position.

Lead Soap Formations - Figure 5 is a photomicrograph illustrating the formation of lead soaps. It will be seen that their needlelike structure adds mechanical strength to a paint film as a wire mesh might contribute mechanical strength to reenforced concrete.

Moreover, the breakdown chemical reaction of the paint vehicles are arrested by the presence of white lead in a paint, for example, such breakdown acids as hydrochloric acid, acetic acid, propionic acid, aldehydes and other breakdown products are neutralized. If these acids were permitted to remain or to increase without forming compounds with lead, the film would break down prematurely.

Zinc Soap Formation - See Figure 6.* Both photomicrographs were taken at the same magnification. Note the shortness of the zinc soap crystals compared to the lead soap crystals. Zinc oxide also forms compounds with the breakdown acids of the paint vehicles and does this selectively without any preference for lead. Therefore, the proper balance between zinc oxide and white lead to provide optimum results in a paint film is a necessity.

Figure 7* describes the tensile strength characteristics of three straight pigmented films. It will be noted that the straight white lead film enjoys the greatest strength over its life of exposure.

Figure 8* illustrates the soap formation of basic silicate white lead 45%. This is a basic new development and has all the good properties of white lead. However, the structure of this pigment was designed by research to concentrate the active part of the pigment on the surface of the particle.

The heavy dark border shown on the crystal edges of Figure 9* comprises basic silicate white lead, which is concentrated at the surface of the crystal.

Figure 10* is a drawing to set forth that the active material in basic Silicate white lead is at the surface and that the core is substantially inert silica. This development provides a pigment for the paint manufacturer, which is economically important. The product is lighter than white lead and yet due to the concentration of the active basic white lead on the surface of the crystal the paint manufacturer can use this compound with equally as good result.

Plastics and the Lead Industry - Vinyl chloride polymers and co-polymers. Although vinyl chloride was polymerized into a resin in 1838 in France, the development did not take hold in this country until about 1939-1940. The delay was due largely to the lack of knowledge as to how to prevent the vinyl chloride from breaking down under heat and light.

The National Lead Company started working with two companies on an experimental basis beginning in 1941 and after learning the necessary chemistry involved in making plastics, we developed a number of organic lead compounds, all of which would stabilize vinyl chloride polymers to a more or less degree.

The chemistry here is much the same as I explained regarding white lead and its function in stabilizing a paint film. In this case the lead reacts with the breakdown acids, mainly hydrochloric acid. Figure 11* shows the effect of a lead stabilizer compared to vinyl plastic containing no stabilizer.

Figure 12* shows the same material exposed to Florida sunlight for one year with and without a lead containing stabilizer.

Figure 13* shows the number of applications to which the vinyl plastics are now being put, such as floor coverings, handbags, upholstering cloth, and wearing apparel.

Figure 14e illustrates a number of commercial or industrial items which are lead stabilizers for vinyl plastics.

Some of the items shown in Figure 15e are: garden hose, water pipe, beer hose, coaxial cable, light and heavy gauge tubing.

Figure 16e shows some of the rigid and semi-rigid materials being made with vinyl plastics, such as phonograph records, of which I am advised 400,000,000 are produced each year and the market is still growing.

Figure 17e describes a test boat LT 532. It sets forth the use of vinyl vehicle paints. The boat was painted about 3½ years ago - August 1946, and inspected February 16, 1950.

Three coats - #1 is a wash coat of pigmented phosphoric acid
#2 is a vinyl copolymer pigmented with red lead two coats

Last coat is a vinyl copolymer pigmented with cuprous oxide.

The unusual thing about this job is, the corrosion and fouling after 3½ years has been substantially nil.

The ratings after 3½ years are about 80-90% of the original coating. Normally under the conditions of test the rating would be about 40% of the original paint.

Specifications for vinyl copolymer vehicles containing red lead are now being prepared in cooperation with the Navy, Coast Guard, and U.S. Maritime Commission.

In closing I should like to say a word about research. I should like to remind you that research is not "directed" - it is where you find it, like gold, or let us say lead, and when you find it, "the idea", the important step is to culture it, and develop it until you have something useful to serve the public.

Fig. 5

Fig. 3

Fig. 1

Fig. 6

Fig. 4

Fig. 2

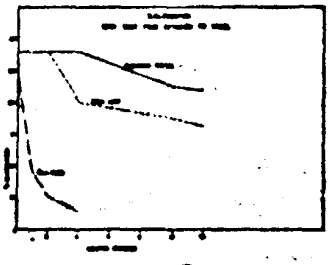

Fig. 7

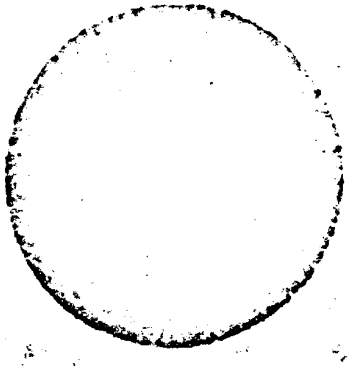

Fig. 8

Fig. 9

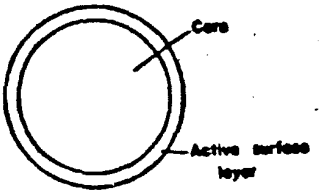

Fig. 10

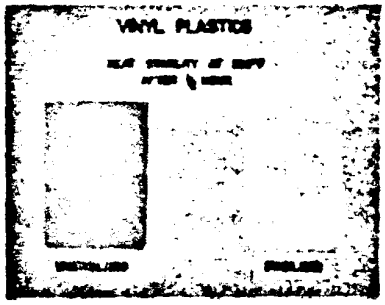

Fig. 11

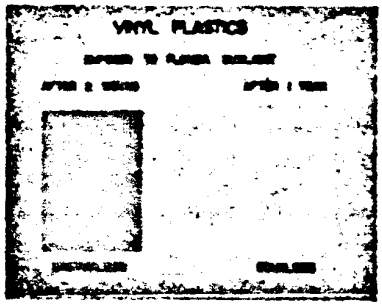

Fig. 12

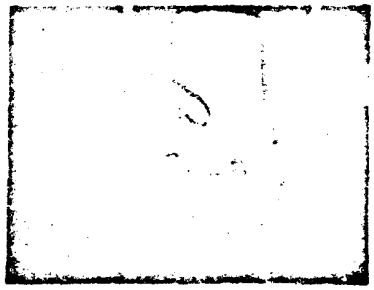

Fig. 13

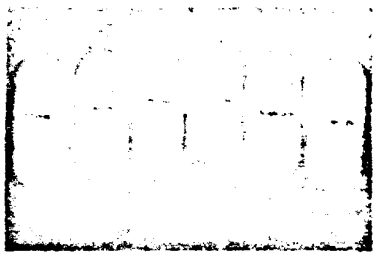

Fig. 14

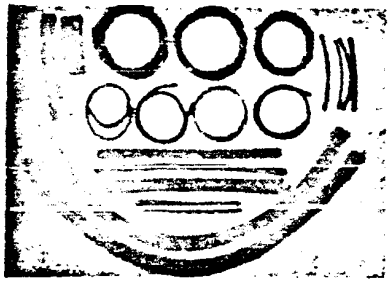

Fig. 15

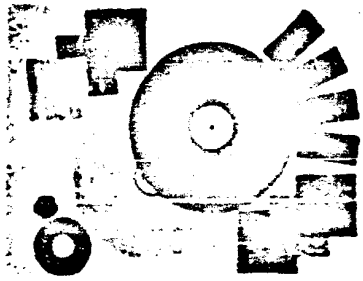

Fig. 16

Fig. 17