LEAD-FREE COATINGS

Charles A. Burger
Laboratory Manager, New Brunswick
Cincinnati Milacron Chemicals Inc.

The Coatings Industry is confronted not only with Federal regulations but also municipal ordinances which make it an offense to sell, supply or offer for sale any coating for use in or around the household if it contains lead metal in excess of 0.5% or, in some areas, as low as 0.06%, based on the total weight of the contained solids or the dried film. Such paints and similar surface coating materials will be banned as a hazardous substance if shipped in interstate commerce.

These restrictions mean that paint manufacturers must avoid incorporating lead compounds such as driers and lead-based feeder products traditionally used to prevent loss of dry during shelf storage. However, paint manufacturers cannot afford the risk of knowingly or purposely adding lead to their products when it is possible that the threshhold level may have been reached by contamination and impurities introduced by other raw materials in the formulation.

The prospect of reviewing and revising drier systems is not one welcomed by the average paint manufacturer. However, reformulating enables the coatings chemist to replace, with confidence, a familiar chemical such as lead drier with Zirco, an equally familiar and accepted catalyst which has been used successfully for 20 years for this very purpose.

Zirco Drier Catalyst 6% is an oil-soluble polymeric zirconyl complex of a synthetic organic acid. When administered orally to white rats it has an LD_{50} of 6,800-10,000 mg./kg. body weight. The intraperitoneal LD_{50} is 1,700-3,400 mg./kg. body weight of albino rabbits.

According to F.D.A. 21, C.F.R. 121.2514, Zirco is permitted as a constituent of resinous and polymeric coatings where these coatings are used as the food contact surface of articles intended for use, among other things, for holding of food. It is neither GRAS nor prior sanction material, but separately investigated and considered a food additive. It may very well be the least toxic of any of the coatings raw materials in use today.

In order to understand the application possibilities of this metal complex, it is important to consider the role of zirconium in its relationship to other driers. It is normally used with other driers in coating systems which rely upon the catalytic effect of certain metallic salts to convert what can be best described as a pourable mixture of pigments, vehicle and solvents to a durable protective and decorative film.

To begin with, it should be stressed that zirconium is not a drier per se, but a drier catalyst and its function is to extend the functional capacity of standard drier metals. In so doing, it exerts a pronounced effect upon the chemical reaction which occurs during the film formation process. This activity affects both air-dried and heat-cured coating formulations.

Conventional drier systems utilizing cobalt, manganese, calcium, iron, cerium and lanthanum metal combinations perform not as a unit but with each metal contributing its own individual characteristic to film properties. When combined with cobalt, zirconium causes this oxidation catalyst, which normally is considered a surface drier, to extend its catalytic activity thmughout the thickness of the film. In this way, drying is achieved without the assistance of any other metal such as lead. Zirconium has an equally beneficial and bifunctional effect upon manganese. It increases the desirable through drying properties of manganese and simultaneously increases the surface drying potential of this metal. Similar synergistic effects are evident with other metals such as calcium, iron and rare earths.

Calcium salts have been employed successfully for many years with manganese and cobalt as a replacement for lead. The function of calcium is best described as an auxiliary drier which will produce some improvements in the physical properties of the dried paint film such as gloss, hardness and, in some instances, through dry. Calcium is also useful as a wetting agent and dispersion aid if incorporated with the pigments during grinding.

However, calcium is not universally dependable as a replacement for lead and its function and applicability is somewhat limited. Zirconium, on the other hand, because of its synergistic influence on all drier metals including calcium has proved to be a consistently dependable lead drier replacement.

The importance of a proper balance of drier metals in any given coating formulation cannot be over-emphasized. This fact is especially critical when zirconium systems are devised. Optimization of zirconium should be sought in order to obtain maximum benefits and usually this is best achieved by laboratory evaluation. Such an approach can be time consuming unless some guidelines are provided. Actually, there is no precise mathematical equation that permits computation of the exact amount of zirconium metal required for the replacement of lead. Fortunately, most paint formulators have been exposed to the Zirco concept of lead replacement and therefore it is not a totally new or unfamiliar experience. Generally recommended is an orderly laboratory evaluation, using gradient levels of zirconium metal consisting of 0.03%, 0.06%, 0.08%, 0.10%, 0.15% and 0.20% based on vehicle solids. As a rule, the major part of the primary drier system remains intact except for the exclusion of lead.

There are cases where a drier system is over complicated and can be simplified by eliminating unnecessary metals that may not be contributing anything to drying performance. Usually a two or three metal component system will suffice. For example, cobalt/zirconium or manganese/zirconium modification of either of these systems with calcium in the range 0.05 - 0.20% may provide additional benefits in the curing schedule. Frequently a combination of cobalt/manganese/zirconium will provide a more desirable balance of activity. Again, much depends upon the vehicle system and the performance requirements of the coating. Also, the replacement of lead by zirconium may result in some benefits that would be difficult to achieve by any other method except perhaps a total reformulation of the coating.

While experienced formulators will generally agree that lead drier has served a necessary and useful purpose in promoting through drying of the paint film, they also recognize that this very characteristic as a strong sustaining polymerization catalyst, is a prime contributing factor to many film failures and deficiencies. Among some of the film failures are embrittlement, poor impact resistance and a subsequent reduction in long-term flexibility and adhesion. Moreover, lead has the inherent disadvantage of being the least compatible of all the metallic soaps and due to its high stoichiometric basicity is likely to react with oils and resins to form insoluble lead soaps. This will adversely affect clarity in clear varnishes and in pigmented systems will produce hazing and loss of gloss. Yellowing and sulfide staining in whites and pastels is a typical phenomenon stemming from high percentages of lead drier.

Just the opposite is true of zirconium, which has traditionally been used to overcome these deficiencies without any sacrifice in the drying performance of the coating. Long-term use of zirconium in all types of architectural and industrial finishes has repeatedly demonstrated that not only will it maintain or improve the curing schedule but very often zirconium will also enhance gloss and gloss retention and eliminate such defects as wrinkling, hazing, yellowing, loss of adhesion and embrittlement of the film after application.

One of the critical questions arising from substitution of lead drier is whether drier loss will occur during shelf storage of certain pigmented systems. Tests indicate that zirconium does not cause loss of dry in those paints where drier loss has never been a problem. If formulators separate those coatings in which feeder driers were used as insurance only from those where a real problem existed and only lead minimized the difficulty, they find that the overall situation may not be as critical as first feared.

Probably one of the most common causes of loss in drying activity is through absorption of driers by pigments. Since zirconium is a poor pigment wetting compound, it is relatively free from absorption by pigment and therefore is always available to the mechanism of the drying process. Even if a small portion of the primary drier is lost through pigment absorption or as a result of some other chemical or physical phenomenon, there is normally sufficient drier remaining for zirconium to catalyze and thus maintain to a large degree most of the original drying schedule.

In many cases it is possible to compensate for some of this loss of primary drier activity by increasing the cobalt metal concentration as much as 50% above the level generally required for adequate drying and in combination with zirconium the risk of wrinkling or a sacrifice in the long-term protective performance of the film due to oxidative destruction or deterioration is eliminated. Another technique is the use of calcium at a level of 0.1% or 0.2% metal based on vehicle solids incorporated in the grind. Calcium at these levels will serve a dual function by aiding pigment dispersion and acting as a sacrificial metal being preferentially absorbed by the pigments thereby reducing the tendency to absorb cobalt or manganese. Iron naphthenate is also useful in this respect but only in formulations where the color it contributes can be tolerated. In addition, there is a large selection of pigment dispersants and wetting agents which will help minimize drier absorption by increasing the capacity of the pigment to absorb vehicle instead of the drier.

Over-grinding should be avoided and not continued beyond the time when adequate dispersion of the pigment is achieved. Temperature of the batch should be kept as low as possible during processing and all driers, except where calcium or iron are incorporated as a grinding aid, should be added last after the batch has been let down with all remaining ingredients and cooled to as close to room temperature as feasible. Whenever possible lower oil absorption demand pigments and extenders should also be used.

All of these techniques, either singly or in combination, have been employed in commercial production to diminate drier loss and are valid approaches to maintaining drying activity during prolonged storage.

Even under the best conditions it is not unusual for a coating to show some lengthening of the drying time by possibly several hours. Unless a dry time specification is involved where maximum limits are imposed, a paint which reaches a tack free state within a 24 hour period is acceptable. Loss of dry becomes a problem only when surface tackiness persists for several days.

Experience indicates that the most critical drier loss problems will occur within two months after the coating has been packaged. In some extreme cases, the problem may become evident within one week. If no loss in drying activity takes place within the first 4-6 months, the probability that a critical situation will develop suddenly is remote.

There is no reliable accelerated laboratory method for predicting drier loss. The best procedure, however time consuming, is to store the paint at prevailing temperatures in the range of 21°C. to 30°C. and to determine periodically over a 12 month period whether there is any change in the drying schedule. Some attempt should be made to control test conditions in terms of temperature and humidity so that environmental variables can be kept to a minimum.

Attempts to accelerate aging by storing paint for 1 to 4 weeks at an elevated temperature of perhaps 49°C. may produce erratic data. First of all, there is no relationship with which to make a prediction that so many days or weeks at 49°C. is equivalent to X number of months of years under actual storage conditions in a paint store or warehouse. Too many side reactions may take place during sustained elevated temperatures that would never occur under average storage conditions. Such reactions result in erroneous conclusions that loss in drier activity can be anticipated. The best that can be said for such a test is that if no loss of dry occurs following storage at elevated temperatures then perhaps drier stability will not be a problem.

The difficulty involving drier absorption does not lend itself to a simple solution due to variations in types of vehicle used. This is especially true with pigments that are prime offenders, notably, carbon blacks, iron oxides, iron blue and toluidene red. It should be pointed out that the extent of drier absorption can be affected by deviations in the composition of each raw material. In some instances, the moisture content of a raw material would be sufficient to alter absorption characteristics.

Aside from all the technical aspects of drier reformulation, another concern of the paint manufacturers is that in order to comply with lead restriction legislation, the cost of producing a gallon of paint may be higher.

Considering the drier situation only (excluding lead-containing pigments) where zirconium is substituted for lead, the cost of a gallon of paint will not necessarily increase. The cost can and will vary in either direction and, in many instances, there will only be minimal changes. In fact, taking a fresh look into drier systems may prove very enlightening. To illustrate, over the years, many drier combinations have become unnecessarily expensive and complicated. The usual procedure has been that when a problem arose where a production batch didn't dry properly or other film defects appeared requiring some fast remedial action, the additive, whether it was in the form of more drier or some other control chemical, automatically became a permanent part of the batch ticket or formula, thus another added cost.

When these drier systems are reviewed and reformulated with lead-free combinations designed for optimum performance the paint manufacturer may find to his surprise that careful selection of drier metals and concentrations has actually resulted in a lowering of the drier cost per gallon of paint. There will inevitably be a number of cases where drier costs will remain unchanged or will increase, but increases will not be such that they produce an unbearable burden on manufacturing costs.

No discussion of zirconium would be complete without raising the question of whether zirconium-based products will someday face the same scrutiny by environmentalists as lead-based compounds. It is highly improbable that zirconium compounds will ever be considered hazardous in coating formulations for zirconium and its salts generally have low systemic toxicity. Zirconium carbonate, zirconium oxide and zirconyl chloride are useful in dermatitic ointments and antiperspirant preparations.

According to "Dangerous Properties of Industrial Materials", third edition, N. Irving Sax, editor, pg. 1249, D. Van Nostrand Co., "Zirconium is not an important poison and as far as is known, the inherent toxicity of zirconium compounds is low."

In summary, any coating normally dependent upon the catalytic activity of driers to promote the oxidation - polymerization mechanism of film formation will respond favorably to zirconium. Careful optimization of the standard drying metals in combination with Zirco will produce a coating film whose protective and decorative function is equivalent, if not superior, to, those combinations employing lead soaps. This can be accomplished without a drastic escalation in cost and, in many cases, the drier cost per gallon of paint is reduced.

There is detailed information available regarding the Zirco approach to lead-free drier systems based on twenty years extensive experience with a broad range of commercially produced coating formulations.

GLD012670

##########