Kirk-Othmer Encyclopedia of Chemical Technology.

DRIERS AND METALLIC SOAPS

Metal soaps as a class of compounds have been defined as the reaction products of alkaline, alkaline-earth, or transition metals with monobasic carboxylic acids containing 6–30 carbons. Commercially important metal soaps include those of aluminum, barium, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, potassium, nickel, zinc, and zirconium. Their solubility or solvation in a variety of organic solvents accounts for their many and varied uses. Significant application areas for metal soaps include lubricants and heat stabilizers in plastics as well as driers in paint (qv), varnishes, and printing inks. Other uses are as processing aids in rubber, fuel and lubricant additives, catalysts, gel thickeners, emulsifiers, water repellents, and fungicides.

The first use of metallic soaps as drying promoters was not actually recorded, but it is clear that improved drying characteristics in vegetable oil coatings became associated with some of the natural earth colors used as pigments and hence small quantities of these pigments were added, not for coloring purposes, but for improving the drying properties. Deliberate use was practiced during the early Egyptian civilization, or at least as early as 2000 BC. The useful materials were various compounds of lead, iron, and manganese, which had sufficient reactivity to form soaps with the fatty acids in vegetable oils. Deposits taken from the axle of a chariot dating back to 1400 BC contained quartz, iron, and a sufficient quantity of fat and lime to indicate the use of a lime soap as a lubricant. There is also evidence of the use of lead in combination with oils in mummification (1).

Early efforts to prepare metal soaps involved attempts to dissolve the natural materials in oils. By the latter part of the nineteenth century, substantial progress had been made in the preparation of fused resinates and linoleates of lead and manganese. The utility of cobalt as a drying catalyst was discovered close to the turn of the century, but the factors that led to its ultimate discovery are not recorded.

Whereas the addition of early metal soaps to a coating for the specific purpose of improving the drying performance did so, the compounds lacked uniformity of composition and therefore did not give predictable results. Even if all of the metal reacted with the acid to give an expected metal ion concentration, which seldom happened, the ions were subject to oxidation, which resulted in loss of solubility in the vehicle and therefore a loss of activity.

A significant advance in metal soap technology occurred in the 1920s with the preparation of the metal naphthenates. Naphthenic acids (qv) are not of precise composition, but rather are mixtures of acids isolated from petroleum. Because the mixture varies, so does acid number, or the combining equivalent of the acid, so that the metal content of the drier would not always be the same from lot to lot. The preparation of solvent solutions of these metal naphthenates gave materials that were easy to handle and allowed the metal content to be standardized. Naphthenates soon became the standard for the industry.

Octoates were the next drier development. Because these driers are produced from synthetic 2-ethylhexanoic acid, the chemical composition can be controlled and uniformity assured. Also, other synthetic acids, eg, isononanoic and neodecanoic, became available and are used for metal soap production. Compared to naphthenic acid, these synthetic acids have high acid values, are more uniform, lighter in color, and do not have its characteristic odor. It is also possible to produce metal soaps with much higher metal content by using synthetic acids.

Table 1. Properties of Solid Metal Soaps[a]

Compound	CAS Registry Number	Total ash	Free fatty acid	Sp gr	Mp, °C	Color	Fineness, μm[b]
Stearate							
Al	[637-12-7]	5.5–16.0	3.0–3.5	1.01	110–150	white	95 – 98% <74(– 200)
Ba	[6865-35-6]	19–28	0.5–1.0	1.23	dec	white	<44(– 325)
Ca	[1592-23-0]	8.8–10.6	0.5	1.12	145–160	white	<44(– 325)
Cd	[2223-93-0]	19.0	0.5	1.21	104	white	99% <74(– 200)
Co	[13586-84-0]	8.2	2.0	1.13	140	violet	99% <74(– 200)
Cu	[660-60-6]	14	1.0	1.10	112	blue-green	99% <44(– 325)
Fe	[2980-59-8], [555-36-2]	13	4.0	1.12	100	red-brown	99% <74(– 200)
Pb	[7428-48-0]	30.2–57.0	0.1–0.6	1.34–2.0	103–dec	white	<74(– 200)
Li	[4485-12-5]	2.5	nil	1.01	212	white	99% <149(– 100)
Mg	[557-04-0]	8.0	0.5	1.03	145	white	<44(– 325)
Mn	[10476-84-3]	12.5	1.0	1.22	110	light brown	99% <74(– 200)
Ni	[2223-95-2]	9.4	5.2	1.13	180	green	<44(– 325)
Sr	[10196-69-7]	17.5	0.5	1.03	155	white	<44(– 325)
Zn	[557-05-1]	13.5–17.7	0.5–0.9	1.09–1.11	120	white	<44(– 325)
Octanoate							
Al	[6028-57-5]	15.7	3.0	1.03	dec	white	98% <74(– 200)
Li	[16577-52-0]	4.7	nil	1.01	dec	white	<149(– 100)
Oleate							
Al	[688-37-9]	10.0	8.5	1.01	134	cream	85% <74(– 200)
Palmitate							
Al	[555-35-1]	8.3	12.5	1.01	120	white	97% <74(– 200)
Zn	[4991-47-3]	14.7	1.4	1.12	123	white	<44(– 325)

[a] Ref. 2.

[b] U.S. standard sieve in parentheses.

More recently, so-called overbased driers with even higher metal contents have become available. These driers are made with combinations of monocarboxylic acids and carbon dioxide or polyfunctional acids.

1. Composition and Properties

Metal soaps are composed of a metal and acid portion supplied as solutions in solvent or oil. The general formula for a metal soap is $(\mathrm{RCOO})_x$. In the case of neutral soaps, x equals the valence of the metal M. Acid soaps contain free acid (positive acid number) whereas neutral (normal) soaps contain no free acid (zero acid number); that is, the ratio of acid equivalents to metal equivalents is greater than one in the acid soap and equal to one in the neutral soap. Basic soap is characterized by a higher metal-to-acid equivalent ratio than the normal metal soap. Particular properties are obtained by adjusting the basicity.

Properties are furthermore determined by the nature of the organic acid, the type of metal and its concentration, the presence of solvent and additives, and the method of manufacture. Higher melting points are characteristics of soaps made of high molecular-weight, straight-chain, saturated fatty acids. Branched-chain unsaturated fatty acids form soaps with lower melting points. Table 1 lists the properties of some solid metal soaps.

The anion used to prepare the metal soap determines to a large extent whether it will meet fundamental requirements, which can be summed up as follows: solubility and stability in various kinds of vehicles (this excludes the use of short-chain acids); good storage stability; low viscosity, making handling the material easier; optimal catalytic effect; and best cost/performance ratio.

2. Manufacture

Metallic soaps are manufactured by one of three processes: a fusion process, a double decomposition or precipitate process, or a direct metal reaction (DMR). The choices of process and solvent depend on the metal, the desired form of the product, the desired purity, raw material availability, and cost.

2.1. Fusion Process

In the fusion process, a metal oxide, carbonate, or hydroxide reacts with a carboxylic acid at temperatures up to 230°C. Water is split out and the resulting metal soap is solubilized in a hydrocarbon solvent because the metal soaps themselves are generally hard, glassy, and difficult to grind.

$$\mathrm{MO} + 2\,\mathrm{RCOOH} \longrightarrow \mathrm{M(OOCR)_2} + \mathrm{H_2O}$$

or

$$\mathrm{M(OH)_2} + 2\,\mathrm{RCOOH} \longrightarrow \mathrm{M(OOCR)_2} + 2\,\mathrm{H_2O}$$

2.2. Double Decomposition

In the double decomposition reaction, an inorganic metal salt such as a sulfate, chloride, acetate, or nitrate reacts with the sodium salt of the carboxylic acid in a hot aqueous solution. The metal soap precipitate is filtered, washed, dried, and milled.

$$\mathrm{NaOH} + \mathrm{RCOOH} \longrightarrow \mathrm{RCOONa} + \mathrm{H_2O}$$

and

$$2\,\mathrm{RCOONa} + \mathrm{MCl_2} \longrightarrow \mathrm{M(OOCR)_2} + 2\,\mathrm{NaCl}$$

2.3. Direct Metal Reaction

The DMR process is carried out over a catalyst with fatty acids in a melted state or dissolved in hydrocarbons. The acid reacts directly with the metal, supplied in a finely divided state, producing the metal soap and in some cases hydrogen. Catalysts include water, aliphatic alcohols, and low molecular-weight organic acids.

$$2\,\mathrm{RCOOH} + \mathrm{M} \longrightarrow \mathrm{M(OOCR)_2} + \mathrm{H_2}$$

The DMR process has no aqueous effluent, gives high purity products, and is less expensive. However, if hydrogen is produced, it has to be removed carefully and should not reach explosive limits. Not all metals are sufficiently reactive to be suitable for the DMR process.

Basic metallic soaps are prepared by overbasing. That is, a normal metallic soap is treated in the presence of excess metal, metal oxide, hydroxide, or various salts, with reactive species, such as CO_2 or SO_2, capable of forming covalent bonds with the metal. The resulting moiety generally contains metal–oxygen bonds free

Table 2. U.S. Production[a, b] of Stearates as Metal Soaps, 10^3 t

Year	Al	Ba	Ca	Mg	Zn	Other	Total
1976[c]	1.10	0.45	20.64	2.51	10.09	1.64	36.59
1977	1.50	0.36	22.91	2.27	12.09	2.37	41.52
1978	1.50	0.32	24.66	2.94	12.11	1.25	42.78
1979	1.65	0.27	24.08	2.97	10.78	1.42	41.17
1980	0.55	0.30	19.94	2.48	7.80	2.53	33.60
1981	0.93	0.47	20.78	6.77	10.54	5.69	45.18
1982	0.83	0.61	26.14	7.71	8.13	1.33	44.75
1983	1.81	0.52	29.46	9.50	10.10	1.09	52.46
1984[d]	1.79	0.28	32.31	10.79	12.84	0.70	59.01
1985[e]	1.46	0.40	31.35	10.26	12.66	0.87	57.27
1986	0.63	0.92	26.62	2.99	11.82		
1987	0.83	0.76	34.97	11.60	15.15		63.40
1988	2.17	1.12	39.86	9.57	16.55	1.80	71.07

[a] Courtesy of Synthetic Organic Chemicals, U.S. Production and Sales, U.S. International Trade Commission.

[b] Less than 100 t of cadmium stearates produced in all years except 1986 for which production was 350 t.

[c] Also 160 t cobalt stearates.

[d] Also 250 t cobalt stearates.

[e] Also 230 t cobalt stearates.

Table 3. U.S. Production of Naphthenates as Metal Soaps, 10^3 t

Year	Ca	Co	Pb	Mg	Zn	Cu	Other	Total
1976	0.38	1.31	2.10	0.45	0.44	0.41	0.44	5.53
1977	0.51	1.70	2.22	0.70	0.60	0.58	1.29	7.60
1978	0.30	1.68	1.84	0.36	0.84	0.54	0.85	6.41
1979	0.37	1.41	2.92	0.39	0.87	0.73	1.26	7.95
1980	0.34	1.07	2.33		0.81	1.01	1.30	6.86
1981	0.22	0.97	1.80		0.61	0.16	1.25	5.01
1982	0.22	0.94		0.14			2.27	3.57
1983	0.31	1.23		0.27		1.45	2.93	6.19
1984	0.21	1.50		0.26		1.36		na
1985	0.22	1.64		0.28		1.60	2.54	6.28
1986	0.23	1.71		0.21		na	2.34	4.49
1987	na	1.41	na	na	na	1.67	2.07	5.15
1988	na	1.26	na	na	na	1.55	2.15	4.96

of carboxy groups. Overbasing can be carried out simultaneously with the general manufacturing techniques although the fusion and DMR processes are preferred; it can also be used as a post treatment.

3. Economic Aspects

Production figures for metal soaps are given in Table 2, 3, 4, 5.

Table 4. U.S. Production[a] of 2-Ethylhexanoates as Metal Soaps, 10^3 t

Year	Ca	Co	Pb	Mn	Zn	Zr	Other	Total
1976	1.14	2.00	1.18	0.45	0.68	1.18	0.82	7.45
1977	0.90	2.00	0.86	0.63	0.71	1.21	1.07	7.38
1978[b]	1.00	2.22	0.97	0.71	0.44	1.26	1.10	7.80
1979	1.07	1.70	0.83	0.58	0.42	1.36	1.55	7.51
1980	0.86	1.33	0.84	0.40	0.36	1.22	1.67	6.68
1981	0.81	1.01	0.54	0.39	0.49	1.12	1.94	6.30
1982	0.73	1.26	0.40	0.37	0.30	1.07	1.57	5.74
1983[c]	1.01	2.46	0.42	0.50	0.28	1.69	2.05	8.75
1984[d]	0.92	2.29	0.49	0.49	0.48	1.49	2.84	9.44
1985[e]	0.97	2.00	0.43	0.49	0.44	1.60	2.71	9.47
1986	1.08	2.38	0.37	0.61	0.42	1.80	2.82	9.48
1987	1.14	2.28	0.38	0.44	0.66	1.95	0.46	7.31
1988	1.26	2.39		0.52	0.60	2.11	4.84	11.72

[a] Courtesy of Synthetic Organic Chemicals, U.S. Production and Sales, U.S. International Trade Commission.

[b] Also 100 t of the Ni soap.

[c] Also 340 t of the Ni soap.

[d] Also 440 t of the Ni soap.

[e] Also 830 t of the Ni soap.

Table 5. U.S. Production[a] of Metal Soaps, 10^3 t

Year	2-Ethyl hexanoates	Stearates	Naphthenates[b]	Tallates[c]	Oleates	Total[d]
1965	1.99	17.02	11.22	3.93	0.13	34.29
1970	na[d]	20.93	12.24	3.75	0.26	39.23
1973	5.16	34.34	9.87	3.38	0.46	53.21
1975	5.39	26.38	5.24	na	0.24	37.25
1977	7.38	41.51	7.57	1.31		57.78
1978	7.80	42.78	6.27	3.67		60.68
1980	6.68	33.61	6.85	2.77		49.91
1981	6.41	45.17	5.01			56.58
1982	5.73	44.75	3.56	1.00		55.04
1983	8.74	52.48	6.19	1.67	0.07	69.13
1984	9.44	59.01	na	1.06	0.17	73.01
1985	9.46	57.26	6.27			72.98
1986	9.25	na	4.49	1.48		na
1987	7.31	63.42	6.16	1.33	0.11	78.33
1988	11.72	71.09	4.96	0.85	0.10	88.72

[a] Courtesy of Synthetic Organic Chemicals, U.S. Production and Sales, U.S. International Trade Commission.

[b] Data include copper naphthenate in all years except 1986.

[c] Data include production of calcium, cobalt, lead, manganese, iron, copper, and other salts.

[d] Certain years (1955–1969, 1973) may include small quantities of palmitates, linoleates, and resinates in the reported total.

4. Analysis

4.1. Metal Content

Two common analytical methods for determining metal content are by titration and by atomic absorption spectrophotometry (aas). The titration method is a complexiometric procedure utilizing the disodium salts of ethylenediaminetetraacetic acid (EDTA). The solvent, indicator, and titrating solution depend on the specific metal being analyzed. In aas the sample is heated to a high temperature in a flame. The flame dissociates the chemical bonds in the metal soap forming a cloud of individual atoms floating in the sample area. In this condition the atoms can absorb radiation. The absorption wavelength differs for each specific element.

4.2. Oxalate Acid Number

A metal soap solution is treated with a measured excess of organic acid. Potassium oxalate solution is added to precipitate the metal and the total sample is back-titrated with alkali to determine its acidity. Acidity is expressed in acid number units, equivalent to mg KOH per g. A neutral soap gives a zero acid number, an acidic soap solution a positive acid number, and a basic soap solution a negative acid number.

4.3. Water Determination

The sample is refluxed with toluene and the resultant toluene–water azeotrope is distilled into a gradual water-trap receiver (Dean and Stark apparatus). Here the water and toluene separate into two distinct layers, permitting the volume of water to be read and its percentage calculated.

4.4. Ash

After the sample is heated in a crucible over a hot plate to drive off volatile solvents and moisture, it is charred over a Bunsen burner and then transferred to a muffle furnace where final ignition is completed. The weight of the ash is determined and reported as a percentage of the weight of the original sample.

4.5. Nonvolatile

A weighed amount of sample is placed in a drying oven maintained at a temperature of 105°C. After three hours, the sample is removed from the oven, placed in a desiccator to cool, and reweighed. The weight of the residue, consisting of solids and nonvolatiles, is calculated as a percentage of the total sample weight taken for analysis.

4.6. Gardner Color

Color measurement is obtained by comparing the sample with 18 separately numbered Gardner color standards. These are conveniently mounted as glass disks on wheels. The entire apparatus, consisting of two wheels containing nine disks each, a case to enclose the wheels, and a slot in the case for the sample, is commercially known as the Hellige Comparator (3).

5. Health and Safety Factors

The hazards encountered in the manufacture, processing, handling, and use of metal soaps are largely associated with the inherent toxicity of the metals and solvents. In general, the acid portion of the metal soap is low in toxicity. Material Safety Data Sheets (MSDS) are available from the commercial suppliers of these metal soaps specifying the inherent hazards. The Hazardous Material Identification System (HMIS) rating for liquid metal soaps may be summarized as follows, where the hazard rating index rates 0–4 as minimal to extreme.

Factor		Rating
health	2	moderate toxicity, may be harmful if inhaled or absorbed
flammability	2	combustible, requires moderate heating to ignite flash point 38 to 93°C
reactivity	0	normally stable, does not react with water

Metal soaps may cause skin irritation or sensitization. They are harmful if swallowed or ingested, which could result in gastrointestinal irritation and vomiting. Inhalation of concentrated vapors can lead to headaches and incoordination.

Solid metal soaps, when finely divided, may present an explosion hazard and are capable of spontaneous combustion. Inhalation of the dust can cause eye and/or respiratory irritation, so they require adequate ventilation.

6. Uses

The principal applications for metal soaps are as heat stabilizers and lubricants (both internal and external) in plastics, and as driers in paint and printing inks.

6.1. Metal Stearates

More than half the metal stearates produced in the United States are applied as lubricants and heat stabilizers (qv) in plastics, particularly in the processing of poly(vinyl chloride) (PVC) resins.

The versatility of PVC allows it to be processed by a number of techniques such as calendering, extrusion, injection molding, blow molding, vacuum, and press forming. However, PVC suffers from a disadvantage in that it has a tendency to degrade on heating or exposure to uv light. Since it is necessary to heat the polymer to relatively high temperatures in order to soften it during the processing operation, this could contribute a limitation to its uses. Heat degradation leads to embrittlement of the plastic and a loss in tensile strength. Incorporation of metallic stabilizers like barium cadmium soaps or calcium zinc soaps into the PVC matrix stabilizes the polymer against the degradation process.

Paper coating applications represent 20% of total demand for metal stearates. Calcium is preferred to aluminum, sodium, ammonium, and zinc stearates (4). Smaller volumes of metal stearates are used in cements (aluminum, calcium, ammonium); drugs, food, and cosmetics (aluminum, calcium, sodium, magnesium, zinc); rubber (zinc, magnesium); grease (aluminum, lithium, zinc); petroleum products (aluminum, lithium, lead, cobalt, manganese); textiles (aluminum, calcium, zinc); and waxes (aluminum, calcium). Their functions in these applications include water repellency, thickening, pigment suspension, gelation, anticaking, flatting, lubrication, and plasticizing (4) (Table 6).

6.2. Metal 2-Ethylhexanoate (Octoates)

The principal applications of metal 2-ethylhexanoates are as paint driers. The drying process of coatings, which contains oxidatively drying vehicles such as air-drying alkyd resins (qv) or drying oils (qv), is characterized by solvent evaporation followed by chemical reactions. This leads to the transition of a liquid to a solid film. The chemical reactions result in oxidative cross-linking and polymerization and are of greatest significance for film formation. Oxidative cross-linking is accelerated and modified through the addition of driers.

Table 6. Applications of Stearates

Function	Cosmetics and toiletries	Food and food packaging	Lacquers and varnishes	Metal working	Paints	Paper	Pharmaceuticals	Plastics
anticaking[a]	Ca, Zn, Mg	Ca, Mg						
antifoaming						Zn, Al		
binding	Mg	Ca, Mg					Mg	
corrosion resisting								
dusting	Zn, Mg							Ca, Zn, Ba
emulsifying	Ca, Zn, Al, Mg	Ca, Mg					Ca	
flatting			Ca, Zn, Al, Mg		Ca, Zn, Al, Mg			
gelling[b]	Al, Mg		Al		Al		Al	Ca, Mg
hardening						Al		
lubrication[a]								
dry				Ca, Zn, Al			Ca, Zn, Mg	Ca, Zn, Mg, Ba
int/ext	Ca, Zn, Mg	Ca, Mg		Ca, Zn, Al, Mg, Ba		Ca		Ca, Zn, Ba
pigment suspen-sion[b]	Mg		Ca, Zn, Al		Ca, Zn, Al			
release[a]	Zn	Ca, Zn, Mg					Mg	Ca, Zn, Al, Mg
sanding sealing			Zn		Zn			
vinyl stabilizing		Ca, Zn						Ca, Zn, Ba
viscosity[b]	Ca, Mg		Ca		Ca, Al			
water repellent	Ca, Zn					Ca, Al		
wetting[b]					Al			

[a] Also, Ca and Zn function in powdered metals.
[b] Also, Al functions in printing inks.

6.2.1. Drier Mechanism

Oxidative cross-linking may also be described as an autoxidation proceeding through four basic steps: induction, peroxide formation, peroxide decomposition, and polymerization (5). The metals used as driers are categorized as active or auxiliary. However, these categories are arbitrary and a considerable amount of overlap exists between them. Drier systems generally contain two or three metals but can contain as many as five or more metals to obtain the desired drying performance.

Active driers. promote oxygen uptake, peroxide formation, and peroxide decomposition. At an elevated temperature several other metals display this catalytic activity but are ineffective at ambient temperature. Active driers include cobalt, manganese, iron, cerium, vanadium, and lead.

Auxiliary driers. do not show catalytic activity themselves, but appear to enhance the activity of the active drier metals. It has been suggested that the auxiliary metals improve the solubility of the active drier metal, can alter the redox potential of the metal, or function through the formation of complexes with the primary drier. Auxiliary driers include barium, zirconium, calcium, bismuth, zinc, potassium, strontium, and lithium.

6.2.1.1. Cobalt. Without a doubt cobalt 2-ethylhexanoate [136-52-7] is the most important and most widely used drying metal soap. Cobalt is primarily an oxidation catalyst and as such acts as a surface or top drier. Cobalt is a transition metal which can exist in two valence states. Although it has a red-violet color, when used at the proper concentration it contributes very little color to clear varnishes or white pigmented systems. Used alone, it may have a tendency to cause surface wrinkling; therefore, to provide uniform drying, cobalt is generally used in combination with other metals, such as manganese, zirconium, lead, calcium, and combinations of these metals.

6.2.1.2. Manganese. Although generally less active than cobalt, manganese 2-ethylhexanoate [15956-58-8] is also an active drier. As an accelerator of the polymerization in baking finishes, manganese is usually more effective than cobalt. Manganese gives better low temperature drying performance than cobalt, and films containing manganese do not suffer from wrinkling under high humidity conditions, as do films with cobalt alone. It also has the advantage that it does not cause baked film to embrittle. As a result of its slower activity, systems prone to skinning can be improved with manganese. It is seldom used alone.

6.2.1.3. Iron. This is a specialty drier that is considered active at temperatures of about 130°C. For this reason iron 2-ethylhexanoate [19583-54-1] is used in bake coatings that require maximum hardness. The principal drawback of using iron driers is that iron contributes a characteristic brownish red color to the coating and should only be used in dark pigmented systems. It has been reported that iron aids the dispersion of carbon black pigment and reduces the tendency for orange peel film defects (6).

6.2.1.4. Cerium/Rare Earth. Cerium 2-ethylhexanoate [56797-01-4] and rare-earth driers promote polymerization and through dry. Like iron they are active at elevated temperature and, since they do not contribute to film discoloration, are recommended for white bake finishes and overprint varnishes where color is critical. Rare earths also find use at the other end of the temperature spectrum in coatings dried at low temperature and high humidity.

6.2.1.5. Lead. Lead 2-ethylhexanoate [16996-40-0] has traditionally been the most commonly used auxiliary drier because it gives excellent through dry in most oleoresinous coatings. It improves flexibility, toughness, and durability of the film. Better water and salt spray resistance is also noted. It also serves as a pigment dispersing and wetting agent, thereby assisting in the dispersion phase of formulating. Use of lead as a grinding aid reduces the tendency for loss of dry.

Because of the toxicity associated with lead compounds, governmental rulings have severely limited the use of lead drier in coatings. From a performance viewpoint the use of lead in aluminum paint will destroy the leafing characteristics of the film. Coatings containing lead that are exposed to sulfur fumes will discolor.

6.2.1.6. Calcium. Calcium 2-ethylhexanoate [136-51-6] has little drying action itself but is very useful in combination with other metals. Calcium driers are also good as pigment wetting and dispersing agents. They help improve hardness and gloss and have been reported to prevent blooming and silking (1).

6.2.1.7. Zirconium. Zirconium 2-ethylhexanoate [22464-99-9] is classified as an auxiliary drier and is the most widely used replacement for lead. Zirconium improves through dry mainly by the formation of coordination bonds. It has excellent color, a low tendency to yellow, and better durability compared to other auxiliary metals.

6.2.1.8. Zinc. The primary function of zinc 2-ethylhexanoate [136-53-8] is to keep the film "open," thus permitting hardening throughout and preventing surface wrinkling. It is an excellent pigment wetting agent and therefore improves pigment dispersion and reduces loss of dry when included in the grind phase of manufacture.

6.2.1.9. Bismuth. Bismuth 2-ethylhexanoate [72877-97-5] is an auxiliary drier that has been promoted for drying under adverse conditions. Like rare earths, in some coatings it is reported to give better results than zirconium at low temperature and high humidity.

6.2.1.10. Vanadium. Vanadium differs from the other drier metals because its greatest stability is at the higher valence state. A considerable disadvantage is its propensity to stain the final film. Vanadium also seems to be particularly prone to loss of dry problems, which again limits its use.

6.2.1.11. Barium. This drier has been used to some extent in Europe as a substitute for lead. Barium 2-ethylhexanoate [2457-01-4] has been under governmental scrutiny because of its fairly acute toxicity.

6.2.1.12. Potassium. Potassium 2-ethylhexanoate [3164-85-0] functions best in conjunction with cobalt. Potassium strongly activates cobalt in aqueous coatings and in high solids paints based on low molecular-weight vehicles.

6.2.1.13. Strontium. Strontium 2-ethylhexanoate [2457-02-5] is a candidate to replace lead in lead-free paints. It functions well under adverse weather conditions and promotes through drying. Outdoor performance of low pigmented coatings like stains may be effected negatively by using strontium instead of zirconium.

6.2.1.14. Lithium. Lithium functions best with cobalt. Lithium 2-ethylhexanoate [15590-62-2] is mainly used as a replacement for lead and in low molecular-weight vehicle, high solids coatings. Lithium promotes through drying and hardness and reduces the sensitivity of high solids coatings to wrinkling.

6.2.2. Water-Borne Coatings

Water-borne air-drying coatings have found a wide acceptance as a replacement for organic solvent coatings. Essentially the same mechanism for drying applies to both water-borne and solvent air-drying vehicles but the drying performance is quite different. Besides the solvent composition, the vehicle system is responsible for various drying deficiencies associated with water-borne coatings, such as slow initial dry time, loss of dry, poor through drying, and hardness (see Coatings).

Water may hydrolyze the vehicle or the metal drier resulting in loss of dry. Water can also slow the oxygen uptake of the vehicle thereby slowing the autoxidation process. Water is considered a strong ligand and complexes metal ions such as cobalt. The resulting complex has a weaker oxidizing potential resulting in a reduction of the performance of cobalt as an autoxidation catalyst.

The vehicle system of water-borne coatings can be divided into two categories: water-emulsifiable vehicles and water-soluble vehicles. Water-emulsifiable vehicles contain emulsifiers that may act as plasticizers after film formation, affecting the hardness. Water-soluble vehicles usually contain a neutralizing amine, the primary purpose of which is to solubilize the resin. These amines can influence the drying properties as they tend to complex the metal drier, thus affecting the catalytic activity. Acceptable results are usually obtained with trialkylamines such as dimethylethanolamine, trimethylamine, and aminomethylpropanol (7).

The differences in composition between water-borne and solvent-borne air-drying paints necessitate change in driers and drier combinations. Since traditional driers are dissolved in mineral spirits, xylene, or other aliphatic/aromatic solvents, they are not readily dispersed in an aqueous system. If traditional driers are used, they must be dissolved in the vehicle before neutralization, which may result in a severe viscosity increase and processing problems.

Traditional driers tend to destabilize emulsified vehicles. The compatibility of these driers with such vehicles is improved by adding suitable surfactants and diluting the drier with cosolvent.

6.2.3. High Solids Coatings

In the coatings industry, many states have or will be placing severe restrictions on the Volatile Organic Content (VOC) of solvent-based enamels. To meet these requirements, a new generation of longer oil and lower molecular-weight alkyd resins are being offered. Although they dry by the same oxidative mechanism, they behave differently from conventional vehicles. The structural variation and lower molecular weight result in slower through dry and/or faster set times with the consequence being soft films and/or possible wrinkling. Other film irregularities such as discoloration or gloss reduction can also occur. Proper selection of the standard metal soaps plus the right balance between active and auxiliary driers is critical in obtaining an acceptable final film.

6.2.4. Loss of Dry

When the initial dry time of a solvent-based coating becomes substantially longer after aging, it is said to lose dry. The primary cause of this problem has been identified as adsorption of the drier on the pigment surface.

Pigments with large surface areas are the worst offenders. There are two common approaches to preventing the phenomenon. The first method is to include a sacrificial drier such as zinc or calcium in the grind as a dispersing agent. The idea is that the sacrificial drier will be preferentially adsorbed on the pigment surface leaving the active driers to function. Another way is to use a "feeder" drier, such as cobalt hydroxy naphthenate, which is not completely soluble but will disperse. Therefore it functions by reacting with the acidity in the vehicle, becoming more soluble as the paint ages, and thereby feeding soluble drier into the paint.

The main reason for loss of dry in water-borne paints is the hydrolysis of the metal soap. In the presence of water the drier is first hydrated. These hydrates are unstable and result in hydrolysis of the metal soap and subsequently the insolubility of the basic metal soap.

6.2.5. Other Octoate Uses

Metal octoates are also used as driers in printing inks. Another application of octoates includes the use of the aluminum salt to gel paint. Stannous, dibutyltin, and bismuth carboxylates find application as catalysts in polyurethane foam applications in order to obtain a reaction efficiency suitable for industrial production. In polyurethane foam manufacture the relative rate of polymerization and gas foaming reactions must be controlled so that the setting of the polymer coincides with the maximum expansion of the foam.

6.3. Metal Naphthenates

Naphthenates of cobalt, manganese, calcium, copper, iron, zinc, and zirconium are used as driers in printing inks. Their use in coatings is declining as a result of the use of higher metal content synthetic driers and the overall trend to latex paint in architectural coatings.

Copper and zinc napthenates are wood preservatives and are of more interest now that there are governmental rules regarding the application of material containing creosote and use of pentachlorophenol. Copper soaps have a good history for protecting wood, textiles, and cordage from decay and mildew. For above ground use, brushing or spraying is adequate. Effective below ground use requires pressure treatment or hot and cold soak treatment. Copper soaps impart a characteristic green color to the treated substrate necessitating the use of zinc soaps when color must be avoided. Zinc soaps are not as effective as copper and must be used in higher amounts.

6.4. Other Metal Soaps

6.4.1. Metal Linoleates and Resinates

The calcium and cobalt salts of linoleates and resinates are used chiefly as components of metallic driers used in printing inks. Copper linoleate [7721-15-5] is used in antifouling paints for marine use (4).

6.4.2. Metal Oleates,Palmitates, and Tallates

Oleate applications include use as driers, fungicides, lubricants, and waterproofing agents. Palmitates are consumed in pigment suspending, waterproofing, and rubber and plastics compounding. Tallate salts are used almost exclusively as paint and printing ink driers (8).

6.5. Other Uses

In the cosmetic, toilet, and pharmaceutical industries, alkali and heavy-metal soaps are employed as ingredients of face powders, talcum powders, tablet formulations, and creams. When added to waxes in candle and crayon manufacture, metallic soaps increase the melting point and prevent softening and sagging at high temperatures. Metal soaps promote adhesion of rubber to steel as required in steel-belted radial tires and similar applications. Because of their hydrophobic nature, metallic soaps are good waterproofing agents.

With the increasing emphasis on energy conservation and environmental considerations, additives for fuels that can correct combustion-related problems have aroused considerable interest. Many commercial fuel additives are combinations of organometallics, dispersants, emulsifiers, and carrier solvents. The organometallic, often a metal soap, acts as a combustion catalyst, increasing efficiency with reduction of smoke, deposits, and corrosion.

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