Utility of Branched Chain Carboxylic Acids in the Manufacture of Driers

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Abstract

To be useful in the manufacture of driers, a carboxylic acid must yield lead, cobalt, manganese, calcium and zinc soaps which are soluble in paint vehicles and petroleum hydrocarbon thinners. The drying metal soaps of a number of saturated branched chain carboxylic acids were prepared to determine the relationship of acid structure to metal soap solubility. It was found that with the exception of 4-ethyl-5,5-dimethylhexanoic acid those branched chain acids containing at least six carbon atoms in the longest straight chain yielded soluble drying metal soaps and were therefore useful in drier manufacture. Soluble "basic" lead soaps, pale-colored manganese soaps and reddish purple cobalt soaps were obtained from acids lacking in alpha branching. Alpha-branched acids yielded insoluble basic lead soaps, dark manganese soaps and dark blue-violet cobalt soaps.

Introduction

Naphthenic acid, tall oil and 2-ethylhexanoic acid are widely used in the manufacture of paint driers. While their chemical structures differ, all three acids have the common characteristic of forming drier metal soaps which are soluble in paint vehicles and petroleum thinners.

Solubility in drying oils and other unsaturated vehicles is necessary for these soaps to function as drying catalysts. Solubility in volatile hydrocarbon paint thinners like mineral spirits is also of importance. When not in solution, the drier soaps are generally brittle or tacky resin-like solids, difficult to handle and to incorporate into paints and varnishes. To overcome this difficulty, drier soaps are supplied commercially as solutions in volatile hydrocarbon solvents at standardized metal concentrations.

Many carboxylic acids have been examined in the past in order to relate their structure to their usefulness in the manufacture of driers. Straight chain saturated acids, like nonanoic (1), decanoic (2), dodecanoic and octadecanoic acids, form lead, cobalt, manganese, calcium and zinc soaps that are insoluble in mineral spirits. Some of these drier metal soaps are soluble in hot or are slightly soluble in cold solvent. However, they must be very soluble both at low and high temperatures to be classified as "soluble" and useful as driers.

Oleic, linoleic and vegetable oil fatty acids composed mainly of these unsaturated acids form oil-soluble drier soaps. Many of them were at one time used commercially in the manufacture of driers. They have been largely displaced by tall oil which contains the same unsaturated acids but is lower in cost.

Polycarboxylic acids form oil-insoluble drying metal soaps and therefore are not suitable as drier acids.

The monoalkyl esters of phthalic and succinic acids form oil-soluble drier soaps when the alkyl group contains at least eight carbon atoms (2). Although the lead soaps of octyl acid phthalate and succinate are soluble in mineral spirits, upon aging the solutions develop precipitates of insoluble lead phthalate and succinate which result from the hydrolysis of the ester group by trace amounts of water usually present. Ester acids as a class are not useful drier acids because of the relative ease with which the ester group hydrolyzes under conditions of manufacture and storage of the drier solutions.

Bruson and Stein (3) synthesized and examined alkylated benzoic acids, alkylated benzoylbenzoic acids and ether acids among others for utility in the manufacture of driers. They found that optimum driers resulted when the alkyl group in the alkylated benzoic and benzoylbenzoic acids contained five carbon atoms. Ether acids of the structure, $RO(CH_2)_nCOOH$, where R is an alkyl group containing more than four carbon atoms and n is a whole number from one to three inclusive, yielded very soluble, useful drier metal soaps. They observed that the manganese soaps of these ether acids were extremely pale in color.

With the exception of the 2-ethylhexanoates, little has been published about the solubility of the drier soaps of branched chain carboxylic acids. This report describes the preparation and solubility of the drier soaps of a number of branched chain saturated carboxylic acids and attempts to relate the structure of these acids to their utility in the manufacture of driers.

Experimental

Materials

The carboxylic acids used are shown in Table I. Based on gas chromatographic and other methods of analysis, the acids were at least 95% pure.

The mineral spirits was Varsol 1 (Humble Oil and Refining Company) containing typically 15% aromatics, 40% naphthenes and 45% paraffins.

The manganous sulfate monohydrate was the Matheson Coleman Bell reagent powder meeting ACS specifications.

The litharge contained 99.5% lead monoxide, the balance consisting of metallic lead, Pb_3O_4 and other materials insoluble in 40% aqueous acetic acid.

The zinc oxide contained 99.5% zinc oxide and 0.5% material volatile at 110C.

The calcium hydroxide contained 97.5% reactive $Ca(OH)_2$ and 2.5% unreactive materials like $CaCO_3$, SiO_2, etc.

The cobalt was a fine powder 99.5% of which passed through a 300 mesh Tyler sieve. It contained 96.6% cobalt metal.

Methods of Preparation

The drier soaps were prepared as solutions in mineral spirits by methods currently employed industrially. Cobalt soaps were prepared by blowing air through a mixture of finely divided metal, acid and mnieral spirits (4). Manganese soaps were prepared by the double decomposition of manganous sulfate and the sodium soap of the acid in the presence of mineral spirits (5). Calcium, lead and zinc soaps were prepared by reacting the acid with either calcium hydroxide, litharge or zinc oxide in the presence of mineral spirits (6). In all cases, when the reaction

TABLE I

Solubility of Drier Metal Carboxylates in Mineral Spirits

Number of carbon atoms	Carboxylic acid	Pb		Co	Mn	Zn	Ca
		Basic	Normal				
6	2-Ethylbutanoic	I	I	S	S	S	S
	2-Methylpentanoic	I	I	S	S	S	S
	4-Methylpentanoic		I	I	I	I	
7	2,2,3-Trimethylbutanoic		I	I	I		
	2,2-Dimethylpentanoic		I	I	S	I	I
	2-Methylhexanoic	I	S	S	S	S	S
8	2-Ethyl-4-methylpentanoic	I	I	S	S	S	S
	2-Ethylhexanoic	I	S	S	S	S	S
9	2,2,4,4-Tetramethylpentanoic		I		S	S	
	2-Propyl-4-methylpentanoic	I	I	S	S	S	S
	3,5,5-Trimethylhexanoic	S	S	S	S	S	S
	4-Ethyl-5-methylhexanoic		S	S	S		
10	4-Ethyl-5,5-dimethylhexanoic		I	S	S	S	S
	4-Ethyl-5-methylheptanoic		S	S	S		
	2-Propylheptanoic	I	S	S	S	S	S

was complete, the reaction mixture was vacuum-dried to remove traces of water and filtered to remove unreacted raw materials or by-product sodium sulfate. The drier solutions obtained were analyzed for metal content and adjusted with additional mineral spirits to contain 6% cobalt, 6% manganese, 24% lead, 5% calcium or 8% zinc.

Stoichiometry

The stoichiometry used in the preparation of the drier solutions varied with the metal. In preparing the cobalt, manganese and calcium driers, a 2:1 mole ratio of acid to metal was employed. A neutral or normal soap was obtained in these cases.

A 1.5:1 mole ratio of acid to metal was employed in the case of the zinc driers. A soap was obtained which corresponded to the empirical formula, $Zn_4O(OOCR)_6$, where RCOO represents the carboxylic acid group. This zinc compound may have the tetrahedral structure suggested by Sidgwick (7) for a basic zinc acetate of the same empirical formula. The zinc atoms are postulated to be positioned at the four corners of a tetrahedron and linked covalently to the unique oxygen at the center while the six carboxylic acid groups span the edges of the tetrahedron. Each acid radical is linked covalently to two zinc atoms through the carboxyl group to form a six-membered ring with the central oxygen atom.

In the case of the lead driers, both normal and basic soaps were prepared. In preparing the normal lead soap, a 2:1 mole ratio of acid to metal was employed. A 1.4:1 mole ratio, such as is generally used to prepare basic lead naphthenate (8), was employed to prepare the basic lead driers. Kastens and Hansen (6) suggested the possibility that basic lead naphthenate has an "anhydride" structure, RCOOPbOPbOOCR. The latter compound may result from the dehydration and condensation of two molecules of an intermediate, RCOOPbOH, previously formed by the addition of one mole of acid to one mole of lead oxide. When a 1.4:1 mole ratio is employed, a mixture of the normal soap, $Pb(RCOO)_2$, and the "anhydride" soap, RCOOPbOPbOOCR, in a 4:3 mole ratio is probably obtained.

Results and Discussion

The solubility in mineral spirits of the drier soaps prepared according to the description given in the experimental section is shown in Table I. Those drier soaps designated as insoluble, "I", precipitated or crystallized completely or incompletely during their preparation or a short time after they were prepared. Those drier soaps designated as soluble, "S", remained in solution for at least six months after their prepartaion. Those driers soaps for which no solubility designation is given were not studied because insufficient carboxylic acid was available for the preparation of all the metal soaps.

It was also observed that mineral spirits solutions of the manganese soaps of 3,5,5-trimethylhexanoic, 4-ethyl-5-methylhexanoic, 4-ethyl-5,5-dimethylhexanoic and 4-ethyl-5-methylheptanoic acids were very pale in color while the cobalt drier solutions of the same acids were reddish purple. All the other acids of Table I, excluding 4-methylpentanoic and 2,2,3-trimethylbutanoic acids, yielded very dark brown manganese and deep blue cobalt drier soap solutions.

Two patterns showing the relationship of the structure of an acid to the solubility and color of its drier metal soaps are evident from the data.

1) Except for 4-ethyl-5,5-dimethylhexanoic acid, branched chain saturated carboxylic acids containing at least six carbon atoms in the longest straight chain yield normal lead soaps which are soluble in mineral spirits.

2) Alpha branching results in insoluble basic lead soaps, deep blue cobalt and dark brown manganese soap solutions.

The first relationship or rule is based on six examples in Table I of soluble lead soaps of acids containing six or more carbon atoms in the longest straight chain. The insoluble lead soap of 4-ethyl-5,5-dimethylhexanoic acid is the only exception. There are eight examples of insoluble lead soaps of acids containing less than six carbon atoms in the longest straight chain. Another example is provided by Chadwick (9) who reported that the lead soap of 2,4,4-trimethylpentanoic acid was only slightly soluble in and crystallized from mineral spirits.

The second rule is based on the insoluble basic lead soaps of 2-methylhexanoic, 2-ethylhexanoic and 2-propylheptanoic acids and nine characteristically colored manganese and cobalt soaps of alpha branched acids. In addition, two commercial acids, one (10) consisting of a mixture of alpha disubstituted C_{10} acids and the other consisting of a mixture of alpha disubstituted C_9, C_{10} and C_{11} acids, were evaluated for utility as drier acids by the author. Both acids yielded insoluble basic (1.4 moles of acid per mole of metal) lead soaps, deep blue cobalt and dark brown manganese soap solutions.

A few examples in Table I indicate that branched chain carboxylic acids containing unsubstituted alpha carbon atoms yield soluble basic lead soaps, pale manganese and reddish purple cobalt soap solutions. Additional examples are provided by acids obtained from the oxo process. An oxo C_{10} acid (11), consisting of a mixture of dimethyloctanoic and trimethylheptanoic acids with closest methyl substitution at the three position, gave a soluble basic lead soap, a pale manganese and a reddish purple cobalt soap solution. Oleic acid also forms lead, cobalt and manganese soaps which resemble those of the alpha-unsubstituted acids. Although not branched, oleic acid may be considered as belonging to this group of acids because it is lacking in alpha substitution.

Another relationship, suggested by a comparison of the soluble cobalt, manganese and zinc soaps of 2-methylpentanoic acid with the corresponding insoluble soaps of 4-methylpentanoic acid, may be that drier metal soap solubility decreases as branching is further removed from the carboxyl group. The validity of this suggested relationship could be established by evaluating 3-methylpentanoic acid and the various positional isomers of methylhexanoic, methylheptanoic acids, etc.

While there is no apparent clear-cut relationship between acid structure and cobalt, manganese, zinc and calcium soap solubility, the first rule generally describes acids which yielded soluble soaps of these metals as well as of lead. Therefore the first rule should be useful in predicting the utility of various branched chain saturated carboxylic acids in the manufacture of driers. On this basis, only four methylhexanoic acid isomers of a total of 16 branched chain C_7 carboxylic acid isomers would be potentially useful in the manufacture of driers. Similarly, 18 structural isomers, comprising ten dimethylhexanoic acids, three ethylhexanoic acids and five methylheptanoic acids, of a total of 38 C_8 carboxylic acids would be potentially useful. Of the 88 branched chain C_9 acids, 57 isomers containing at least six carbon atoms in the longest straight chain would also be potentially useful.

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