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RESINOUS CONDENSATION PRODUCTS FROM METAL ALLOYS AND HYDROCARBON DI-HALIDES

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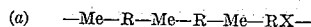
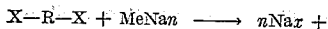
No Drawing. Application June 20, 1952,
Serial No. 294,710

7 Claims. (Cl. 260—2)

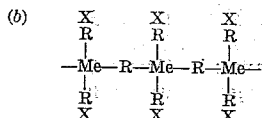
The present invention is a continuation-in-part of my copending application Serial No. 69,617, filed January 6, 1949, now abandoned, and an improvement upon my Patent No. 2,447,926, and relates to heavy resinous materials containing heavy polyvalent metal bonded to hydrocarbon, and to a method of forming the same.

The resinous materials hereof are reaction products of polyvalent heavy metal alloyed with alkali metal with hydrocarbon polyhalide. The specific resinous structure of the materials is not known.

The reaction is exemplified only theoretically by the following equations:



or



where R is monocyclic or 1 to 4 carbon atom aliphatic hydrocarbon, X is halogen, Me is a polyvalent heavy metal forming true alloys with alkali metal and n is the number of valences thereof. The product (a) theoretically illustrates a type of polymer where divalent heavy metal is reacted. Such metals as copper, cadmium, zinc form such resins as shown theoretically in formula (a). Other higher valent heavy metals such as lead, tin, thallium, gallium, indium, zirconium, tantalum, tungsten, molybdenum, uranium, iron, bismuth, cobalt, chromium and nickel, may form cross linking polymers theoretically illustrated by such as product (b) and metals with more than one valence above such as cobalt, nickel, etc., may form mixed polymeric types.

The hydrocarbon base is a hydrocarbon base of a character which does not tend to cyclize such as aliphatic of 1 to 4 carbon atoms or monocyclic aromatic or hydroaromatic and combined cyclic and acyclic types. These hydrocarbon bases are substituted with at least two halogen atoms, but any larger number may be used. The use of a larger number of halogen substituents on the hydrocarbon could theoretically form polymers with metal having a corresponding degree of cross-linking. With decrease in the atomic weight of the hydrocarbon base, the ratio of metal to the remainder of the molecule increases with consequent increase in specific gravity.

For purposes of forming polymers of high specific gravity, low molecular weight alkylene polyhalide base is preferred. For such use, methylene dichloride, methylene dibromide, chloroform, bromoform, or carbon tetrachloride are suitable alkylene polyhalide base molecules. Similarly ethylene polyhalides such as 1-2 dichloroethane, 1-3 dichloropropane, 1-4 dichlorobutane tetrachloro ethane or unsymmetrical trichloro ethane may be used. Similarly polyhalogen monocyclic aromatics and alicyclics including hydrocarbon cyclic bases also having

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lower alkyl substituents wherein the halogen is substituted on the ring or in the side chain or both such as dichlorobenzene, hexachlorocyclohexane, polyhalogenated xylenes, and parachlorobenzyl chloride.

The reaction may also be effected upon polymerizable halogenated unsaturated materials such as polyvinyl chloride, chlorinated rubber, dichlorobutadiene, 1-4, and polyhalogen vinyl acetylene and 1,2 dichloroethylene.

The heavy polyvalent metal to be reacted is first alloyed with an alkali metal such as sodium, potassium or lithium by adding small pieces of the metal to a sodium, lithium, etc. melt. Such polyvalent metals as mentioned above are alloyed with the melted sodium, lithium, etc. and the alloy is cooled and broken into small chips, granules or powder. In such alloy the polyvalent metal is present in greater than equivalent quantity to the halogen to be displaced from the hydrocarbon, but the sodium or lithium is preferably present in quantity to form an 8 to 50% alkali metal such as sodium content of the alloy with the polyvalent metal, preferably about 10 to 15%.

The halogenated hydrocarbon is directly reacted with the polyvalent metal sodium with heat and usually under pressure for one to fifteen hours in an autoclave of 3 to 10 atmospheres, the temperature ranging from 65° to 150° C. with or without an inert solvent such as petroleum ether, hexane, or ligroin. Where the halogenated hydrocarbon is of low volatility, the reaction may be carried out under reflux of the solvent in an inert atmosphere, such as nitrogen or hydrogen.

The reaction may be activated by certain catalysts such as organic or inorganic iodine and iodine compounds, organic acid anhydrides, certain metal alloys such as aluminum containing minor quantities of copper, zinc and iron, inorganic acid such as hydrochloric acid and anhydrous acid salts such as aluminum chloride and boron trifluoride.

Example I

A 10% alloy is first formed by adding powdered lead to molten sodium in proportion to form an alloy containing 10% by weight of sodium. The alloy melt is cooled and granulated. 87 grams of methylene dichloride is dissolved in 500 cc. of n-hexane to which is added 2700 grams of the granulated alloy of lead containing 10% of sodium and 2 grams of elemental iodine. The mixture is placed in an autoclave and heated at 73 to 75° C. for ten hours. At the end of the period the cooled liquid is filtered through active charcoal and the solvent removed by vacuum distillation. The product is a dark amber colored resin having a specific gravity of 6.7. The product is soluble in hydrocarbon naphtha and oils.

Example II

A 10% alloy of metallic tin with sodium is prepared as described in Example I. 100 grams of ethylene dichloride 1,2 is dissolved in 700 cc. n-hexane to which is added 1400 grams of the powdered alloy and the mixture is heated under air free reflux for fifteen hours. The solution and suspended salt are then filtered through decolorizing charcoal, and the solvent is removed under vacuum. The heavy brittle residue obtained has a specific gravity of 5.8, has an amber color and melts on the steam bath to a clean amber colored fluid.

Example III

147 grams of paradichlorobenzene dissolved in 300 cc. of benzene and refluxed ten hours in an air free atmosphere with 35 grams of copper sodium alloy containing 10% of sodium prepared according to the method described in Example I. A brittle yellowish amber resin is obtained after purification and removal of solvent which has a specific gravity of 5.7.

Example IV

80 grams of a 10% sodium alloy with zinc are heated with 164 gr. of ethylene dibromide 1,2 in 500 cc. of n-hexane in an autoclave at 90° C. for 30 hours. A brittle amber colored resin having a specific gravity of 5.2 is obtained after filtering the reaction product and removing the solvent by distillation.

The resins herein, because of their solubility in solvent, particularly hydrocarbon and high specific gravity, are useful additives, weighting agents and filler materials. They may be used as oil well drilling fluid weighting agents for oil type drilling fluids, as radio-paques, as rubber fillers, as blending agents for other resins, as molding powders alone and with other resins and filler materials.

I claim:

1. A resinous material formed by reacting by heating a mixture of an alloy of an alkali metal and a heavy metal selected from the group consisting of copper, cadmium, zinc, lead, tin, thallium, gallium, indium, zirconium, tantalum, tungsten, molybdenum, uranium, iron, bismuth, cobalt, chromium, nickel, with a polyhalogen hydrocarbon compound selected from the group consisting of monocarbocyclic dihalides and dihalides of aliphatic hydrocarbons having 1 to 4 carbon atoms, said heavy metal and dihalogen hydrocarbon compound being in substantially equal molar proportions.

2. The method of forming a heavy metal containing resin, comprising reacting by heating a mixture of an alloy of an alkali metal and a heavy metal selected from the group consisting of copper, cadmium, zinc, lead, tin, thallium, gallium, indium, zirconium, tantalum, tungsten, molybdenum, uranium, iron, bismuth, cobalt, chromium, nickel, with a polyhalogen hydrocarbon compound selected from the group consisting of monocarbocyclic dihalides and dihalides of aliphatic hydrocarbons having 1 to 4 carbon atoms, said heavy metal and dihalogen hydrocarbon compound being in substantially equal molar proportions.

3. The resin defined in claim 1 wherein the metal is lead.

4. The resin defined in claim 1 wherein the metal is copper.

5 5. The resin defined in claim 1 wherein the metal is tin.

6. The resin defined in claim 1 wherein the multivalent hydrocarbon radical is divalentcarbocyclic.

10 7. The resin defined in claim 1 wherein the hydrocarbon radical is a divalent aliphatic radical having 1 to 4 carbon atoms.

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