Superbase zinc soaps in the form of zinc carboxylates, in which the carboxylic acids consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics: a linear acid content of between 0 and 40 % by weight, a content of acids which are branched on carbon 2 of between 0 and 20 % by weight, and a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater than 50 % by weight; their preparation and use as polymer stabilisers particularly for polyvinyl chloride.
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BASIC ZINC CARBOXYLATES.

The present invention relates to new basic zinc carboxylate, both liquid and solid compositions, a method for their preparation and their use as lubricant additives, as polymer stabilisers, as promoters or emulsifiers for rubber and fungicides. In particular the invention provides an effective stabiliser for use in polyvinyl chloride which may replace the more toxic Cadmin, Lead and Barium stabilisers currently used.

Basic zinc carboxylates are known in many forms and are commonly used as polymer stabilisers.

It is desirable to have as high a zinc level as possible in these products to reduce the amount of additive required to provide the desired zinc level. It has however proved difficult to develop a commercial process for the production of high zinc content zinc carboxylates.

There is therefore a need for a high solid content or 100% solid basic zinc carboxylate which may be incorporated into polymers, particularly as a stabiliser for polyvinyl chloride without an adverse effect of the viscosity of the polymer to enable better handling.

We have now found that high zinc contents may be obtained when the various carboxylic acid mixtures described in European Patent 234149 are used as raw materials.

We have now developed new solid zinc superbase soaps which do not possess the disadvantages of the known superbase soaps, which have a high metal content of the order of 15% to 35%, typically 20% to 30% or even higher, and which yield perfectly stable and clear solutions when employed.

The present invention therefore provides solid zinc superbase soaps in the form of zinc carboxylates, the carboxylic acids consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics, optionally the products may also contain zinc carbonate.
- a linear acid content of between 0 and 40% by weight,

- a content of acids which are branched on carbon 2 of between 0 and 20% by weight, and

- a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater than 50% by weight.

The zinc superbase soaps are preferably prepared from saturated C₈, C₉ and C₁₀ organic carboxylic acids which consist of isomeric mixtures and which are generally known as oxo acids. These oxo acids are characterized by a low linear acid content, generally less than or equal to 10% by weight, a low content of acids which are branched on carbon 2, generally less than or equal to 10% by weight, and a high content of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, which is generally greater than 80% by weight. The oxo acids are obtained by hydroformylation of C₇, C₈ and C₉ olefins, followed by an oxidation.

Still more preferably, the zinc soaps according to the invention are prepared from the C₈ saturated carboxylic acid (that is containing 8 carbon atoms) marketed under the trademark Cekanoic, this acid consisting of an isomeric mixture of octanoic acids containing at most 10% by weight of n-octanoic acid, at most 10% by weight of C₈ acids which are branched on carbon 2 and at least 80% by weight of C₈ acids which are branched on carbon 3 and/or the carbons of higher rank. In fact, it has surprisingly been found that the use of this acid makes it possible to obtain zinc soaps with a very high zinc content of the order of 25% or higher. Still more preferably it is made from the similar material known as Cekanoic C₁₀ acid.

Among the organic carboxylic acids which are also suitable for the present invention there may also be added the derivatives which are mono- or polysubstituted in the 3-position and/or of higher rank of the acids corresponding to heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid and dodecanoic acid. These include, for example, 3-methylhexanoic acid, isoctanoic acid, 4,5-dimethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, isodecanoic acid, 3-ethylxctanoic acid, isoundecanoic acid, 4-ethylnonanoic acid and isododecanoic acid. The mixture
of one or more of the above-mentioned acids, whether mixed or not with their
isomers, is also suitable for the present invention, it being understood that the
content of linear acids does not exceed 40% and that the content of acids which
are substituted on carbon 2 does not exceed 20%. We have found, in fact, that
the linear acids and that the acids branched on carbon 2 lead to the formation of
a viscous product, or to setting solid or, alternatively, to a precipitate which
renders the product practically useless.

The present invention also relates to a process for the preparation of the zinc
superbase soaps described above, according to which a zinc oxide and/or
hydroxide is reacted with the appropriate acid, with stirring. In a further
embodiment the reaction may include the addition of carbon dioxide (CO₂) which
is bubbled through the reaction mixture and at least one organic carboxylic acid,
in the presence of at least one promoter which make CO₂ fixation easier and at
least one catalyst, and in that the water formed during the reaction is removed.
In this aspect of the invention the process is characterized in that the reaction is
performed in at least one organic solvent at a temperature of between 80 and
120°C, and in that the said acid is a saturated organic carboxylic acid containing
from 7 to 13 carbon atoms, in which the content of linear acids is less than or
equal to 40% by weight, in which the content of acids branched on carbon 2 is
less than or equal to 20% by weight, and in which the content of acids branched
on carbon 3 and/or the carbons of higher rank is equal to or higher than 40% by
weight.

When the reaction has ended, after filtration, the organic solvent may be
removed preferably by evaporation.

In accordance with a preferred embodiment of the process according to the
invention, the organic solvent is allowed to evaporate during the reaction and is
recycled into the reaction mixture so as to produce therein a bubbling action
which promotes the reaction. Alternatively, a plasticiser ester such as a
phthalate or adipate may be used as the solvent which is particularly useful when
the zinc carboxylate is to be used as a stabiliser for polyvinyl chloride.

At least one nonpolar organic solvent chosen from naphtha, hexane, kerosene,
benzene, toluene or xylene is used among the organic solvents which can be
used in the process according to the invention. It is also possible to use a
mixture of paraffinic hydrocarbons of mineral or synthetic origin, preferably
containing a low proportion of aromatic and/or naphthenic hydrocarbons, such as
white spirit. It is also possible to consider the use of polar organic solvents such
as alcohols, for example 1-butanol, 2-butanol, ethylene glycol, propylene glycol,
ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, diethylene
glycol and its ethers, mixtures of alcohols derived from paraffin, or methyl ethyl
ketone.

The molar ratio of zinc to the organic carboxylic acid employed in the reaction is
generally between 0.55 and 2, which corresponds to a basicity of between 1.1
and 4.

It should be recalled that the basicity is equal to the ratio of equivalents of zinc to
the equivalents of carboxylic acids which are employed.

Where carbon dioxide is used an hourly flow rate of carbon dioxide is imposed
such that the hourly mass ratio of carbon dioxide to zinc is between 0.5 and 2,
and preferably between 0.7 and 1.5.

Among the catalysts which may be used in the process according to the invention
there may be mentioned metal oxides, for example, aluminium oxide Al₂O₃, silver
oxide Ag₂O, magnesium oxide MgO, and zinc carboxylates such as zinc
octanoate.

When CO₂ is used among the promoters which made CO₂ fixation easier and
which can be used in the present invention there may be mentioned labile
hydrogen compounds such as alcohols, for example methanol, 2-propanol, octyl
alcohol, ethylene glycol, triethylene glycol, stearyl alcohol, cyclohexylene glycol
alcohol, cyclohexyl alcohol, aromatic alcohols such as phenol; amines, for
example aniline, phenylenediamine, or dodecylamine; or, yet again, a mixture of
alcohols and/or amines, for example of methanol and aqueous ammonia.

However, preferably, the material used in methanol, which gives the highest
basicities and the shortest filtration times during the preparation of the calcium
soap according to the invention.
In the superbase soaps according to the invention, the promoters are used in a proportion of 1 to 25% by weight of final zinc salt, and preferably in a proportion of 5 to 15%.

The present invention will be better understood by reading the nonlimiting examples of the invention which follow.

Example 1:
94.1 g Zinc Oxide (having a minimum purity of 99.5%) and 123.3 g Diisononyl phthalate were loaded into a reactor and stirred vigorously for 15 minutes. Over a period of 45 minutes 298.3 g Cekanoic C$_{10}$ acid is added and the temperature raised to 27°C, the heater was then set at 30°C and the exothermic reaction took the temperature to 52°C. The solution was slowly heated to 165°C to remove the water from the reactor and maintained at 165°C until no more water comes over.

Example 2
93.9g of the Zinc Oxide used in Example and 127.3 g Diisononyl phthalate were loaded into a reactor and stirred vigorously for 15 minutes. Over a period of 45 minutes 298.2 g 298.2 g Cekanoic C$_{10}$ acid is added and the temperature raised to 27°C, the heater was set at 30°C and the exothermic reaction took the temperature quickly to 52°C. The solution was slowly heated to 110°C and then put vacuum on it to remove the water from the reactor. Filtration was carried out at 110°C to yield the end product as a viscous light yellow liquid.

Example 3
93.8 g of the Zinc Oxide used in Example 1 and 123.6 g Toluene were loaded into a reactor and stirred vigorously for 15 minutes. Over a period of 45 minutes 298.9 g Cekanoic C$_{10}$ acid is added and the temperature raised to 40°C. The solution is then slowly heated to 129°C to remove the water from the reactor and maintained at 129°C until no more water comes over. The end product is a clear product.

The Toluene is evaporated and a white solid paste is formed.
Claims:

1. Solid zinc superbase soaps in the form of zinc carboxylates, the carboxylic acids consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics:
   - a linear acid content of between 0 and 40% by weight,
   - a content of acids which are branched on carbon 2 of between 0 and 20% by weight, and
   - a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater than 50% by weight.

2. The zinc superbase soaps of claim 1 prepared from saturated isomeric mixtures of C₈, C₉ and C₁₀ organic carboxylic acids.

3. The zinc soap of claim 2 in which the oxo acids are characterized by a low linear acid content, generally less than or equal to 10% by weight, a low content of acids which are branched on carbon 2, generally less than or equal to 10% by weight, and a high content of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, which is generally greater than 80% by weight.

4. A process for the preparation of the zinc superbase soaps according to any of claims 1 to 3, according to which a zinc oxide and/or hydroxide is reacted, with stirring, with carbon dioxide (or CO₂) which is bubbled through the reaction mixture and at least one organic carboxylic acid, in the presence of at least one promoter which makes CO₂ fixation easier and at least one catalyst, and in that the water formed during the reaction is removed.

5. A process according to claim 4 is characterized in that the reaction is performed in at least one organic solvent at a temperature of between 80 and 120°C, and in that the said acid is a saturated organic carboxylic acid.
containing from 7 to 13 carbon atoms, in which the content of linear acids is less than or equal to 40% by weight, in which the content of acids branched on carbon 2 is less than or equal to 20% by weight, and in which the content of acids branched on carbon 3 and/or the carbons of higher rank is equal to or higher than 40% by weight.

A process according to claim 4 or claim 5 in which the organic solvent is allowed to evaporate during the reaction and is recycled into the reaction mixture so as to produce therein a bubbling action which promotes the reaction.

The use of a superbase zinc soap according to any of claims 1 to 4 as a stabiliser for polyvinyl chloride.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C53/126 C08K5/09 C07C53/128

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category C Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.

Y EP, A, 0 010 807 (AKZO N.V.) 14 May 1980 see page 11, line 27 - line 38 see claim 1 1-3,7

Y US, A, 3 730 943 (WEISFELD ET AL.) 1 May 1973 see column 2, line 32 - line 71 see column 3, line 44 - line 52 1-3,7

A WO, A, 93 08246 (EXXON CHEMICAL PATENTS INC.) 29 April 1993 see claims 1-5 1

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search 27 September 1995

Date of mailing of the international search report 09.10.95

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