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MANUFACTURE OF POLYVALENT METAL
SOAPS

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This invention relates to the manufacture of
polyvalent metal soaps, and more particularly
polyvalent metal naphthenates from naphthenic
acids such as are obtained from petroleum.

One of the principal objects of this invention
is to provide a method of manufacturing metallic
soaps of this character which is effective to se-
cure a substantially increased yield of improved
product in a simple and expeditious manner.

Other objects and advantages of the invention
will be apparent from the following description
and the accompanying claims.

In the manufacture of soaps such as metallic
naphthenates of this character, it has heretofore
been the practice to effect double decomposition
by the addition to a water solution of an alkali
metal naphthenate of a water solution of a poly-
valent or heavy metal salt to secure a precipitation
of the polyvalent or heavy metal naphthenate with
concomitant production of a salt of the alkali metal
which remains in solution. Considerable diffi-
culty is experienced in the manufacture of cer-
tain polyvalent or heavy metal soaps in this man-
ner, due to the fact that extremely low yields
are obtained, because the metal salt is unstable
in aqueous solution and the double decomposi-
tion reaction does not go to completion under
these conditions.

I have discovered that unexpectedly large yields
are obtained where the polyvalent or heavy metal
salt is added in solid form to the alkali metal
soap solution as opposed to the customary prac-
tice of adding the salt in solution form. This is
directly contrary to the result which would be
expected from the law of mass action, and is ap-
parently explained by the fact that the added
metal of the salt is immediately removed from
the scene of reaction by this procedure, whereas
in the case where a water solution of the metal
salt is employed, secondary reactions or side re-
actions take place which reduce the quantity of
the metal salt available to produce the desired
metallic soap.

The present invention is applicable to the
manufacture of soaps of such metals as tin, iron,
zinc, nickel, chromium, manganese, aluminum,
copper, lead, and the like. For purposes of easy
description, the expression "polyvalent metal" is
hereinafter used throughout the description and
claims to designate metals of this character. As
a further advantage of my invention, in addition
to the substantially higher yield specified above,
it is found that the polyvalent metal soaps pro-
duced have a higher metal content indicating a
purer product. The present invention appears
particularly applicable to the manufacture of
such polyvalent metal soaps in which the metal
exists in the "ous" form, such for example as
stannous, ferrous, cuprous, mercurous and the
like.

Unusually good results have been secured by
this method in the manufacture of stannous
naphthenate, which is described as a preferred
embodiment of the invention. My method com-
prises neutralizing naphthenic acids with a water
solution of an alkali metal base, such as sodium
hydroxide, potassium hydroxide, and the like, to
form a water solution of the corresponding alkali
metal naphthenate. To this solution is then
added in solid form sufficient water soluble poly-
valent metal salt, such as stannous chloride, to
react with the alkali metal naphthenate to pro-
duce a precipitation of polyvalent metal naph-
thenate while forming a water solution of the
alkali metal salt by double decomposition. There-
after, the precipitate is separated from the water
solution. This is effectively accomplished by
adding a water immiscible organic solvent in
which the precipitated polyvalent metal naph-
thenate is soluble, and agitating to dissolve the
precipitated naphthenate in the solvent. Suit-
able organic solvents for this purpose comprise
benzol, toluol, naphtha, and the like. The mix
is then allowed to stand to stratify into a solvent
layer containing the dissolved metal naphthenate
and a water solution layer, and the layers are
then separated as by decantation. The solvent
may then be stripped to recover the metal naph-
thenate.

By way of example, naphthenic acids of com-
paratively high molecular weight obtained from
heavy residual petroleum oil, were employed, said
acids having the following tests:

Neutralization number, 130;
Saponification number, 137;
Ash, 0.15%; and
Non-saponifiable matter, 24.0%

Thirty pounds of the acids were charged in the
reaction kettle with 300 pounds of water, and 6.5
pounds of caustic soda solution (48.5%) were
added. The water to acid ratio of 10:1 as used
above enables the end point of the operation to
be more easily recognized, although it is found
that this ratio may be reduced to 5:1 or less with-
out reduction in yield or character of the prod-
uct. The quantity of sodium hydroxide is cal-
culated to neutralize the naphthenic acids and
form a substantially neutral solution of sodium
naphthenate. The temperature of the kettle was
then brought to 140° F. and 8.7 pounds of solid
stannous chloride crystals were added gradually
over a period of ten minutes with agitation. The
quantity of stannous chloride is calculated to
complete the reaction by double decomposition
of the sodium naphthenate to stannous naph-
thenate; but an excess of stannous chloride is
avoided, since such an excess results in the for-
mation of tin oxychloride which causes increased
difficulty in the clarification of the final product.

By reason of the addition of the stannous chloride in solid form, side reactions which occur with the metal salt in solution, including the production and precipitation of tin oxychloride, are prevented, and substantially all of the tin of the metal salt remains active for reaction with the sodium naphthenate to produce a precipitate of stannous naphthenate.

Following the addition of the solid stannous chloride, 68 pounds of benzol were added at once with continued agitation until the precipitated stannous naphthenate soap had dissolved in the benzol. The mass was then allowed to stand for two hours to stratify into an upper benzene layer and a lower water layer. The water layer was removed and the benzol layer filtered through an inactive clay to clarify the same. The benzol was then stripped off in a vacuum still employing an inert gaseous atmosphere, sufficient vacuum being used so that a maximum stripping temperature of 250° F. was sufficient to remove the benzol. The stannous naphthenate so obtained was a plastic brown liquid of good character and purity, having the following tests:

25	Ash-----	per cent-----	14.73
	Theoretical ash based on neutralization number-----	per cent-----	15.4
	Yield as computed by ratio of ash to theoretical ash-----	per cent-----	96
30	Insoluble in precipitation naphtha-----	per cent-----	0.06
	Neutralization number-----		80

In the above example, it is noted that a yield of 96% of stannous naphthenate based on the calculated theoretical yield from the quantity of naphthenic acids employed was obtained, as compared with yields of the order of about 40% or less when the stannous chloride is added in solution form. While an elevated temperature of the order of about 140° F. was employed in the above example during the precipitation of the stannous soap, it is found that equally good results may be obtained by precipitation of the soap at temperatures varying from normal atmospheric temperatures up to said elevated temperature. It is desirable to maintain temperatures, particularly the temperatures of stripping to remove the benzol, as low as possible in order to preserve the desirable properties and color of the product. For this purpose, a low boiling cutter is employed so that it can be stripped at a comparatively low temperature, particularly with the aid of vacuum.

While the invention has been particularly described above in connection with the manufacture of polyvalent metal naphthenates, it is to be understood that this invention is also applicable to the manufacture of polyvalent metal soaps of other acids, such as the higher fatty acids, including stearic, oleic, palmitic, etc., and mixtures thereof, and also the substituted fatty acids such as the halogenated fatty acids and the like.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the manufacture of a polyvalent metal soap from a water solution of an alkali metal soap, the steps which comprise adding directly to the said water solution a water-soluble polyvalent

metal salt, which tends to decompose in water, in solid form unmixed with water to cause a precipitation of polyvalent metal soap, and separating the polyvalent metal soap from the resulting solution.

2. The method in the manufacture of a polyvalent metal naphthenate which comprises neutralizing naphthenic acids with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate, then adding a water soluble polyvalent metal salt, which tends to decompose in water, in solid form unmixed with water to said solution to cause a precipitation of polyvalent metal naphthenate, and separating the polyvalent metal naphthenate from the resulting solution.

3. The method in the manufacture of a polyvalent metal naphthenate in which the polyvalent metal exists in the "ous" form, which comprises neutralizing naphthenic acids with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate, then adding a water soluble salt of a polyvalent metal in the "ous" form in solid state unmixed with water to cause a precipitation of polyvalent metal naphthenate in the "ous" form, adding a water immiscible organic solvent to the resulting mix to dissolve the precipitated naphthenate in the said solvent, allowing the mix to stratify into a solvent layer containing the dissolved naphthenate and a water solution layer, separating the said layers, and stripping the solvent from the solvent layer to obtain the desired polyvalent metal naphthenate.

4. The method in the manufacture of stannous naphthenate which comprises neutralizing naphthenic acids with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate, then adding a water soluble stannous salt in solid form unmixed with water to cause precipitation of stannous naphthenate, and separating the stannous naphthenate from the resulting solution.

5. The method in the manufacture of stannous naphthenate which comprises neutralizing naphthenic acids with a water solution of sodium hydroxide to form a water solution of sodium naphthenate, then adding stannous chloride in solid form unmixed with water to cause a precipitation of stannous naphthenate, adding a water immiscible organic solvent to the resulting mix to dissolve the precipitated stannous naphthenate in the said solvent, allowing the mix to stratify into a solvent layer containing the dissolved stannous naphthenate and a water solution layer, and separating the said layers.

6. In the manufacture of a polyvalent metal naphthenate from a water solution of an alkali metal naphthenate, the steps which comprise adding to the said water solution a water soluble polyvalent metal salt, which tends to decompose in water, in solid form unmixed with water to cause a precipitation of polyvalent metal naphthenate, and separating the polyvalent metal naphthenate from the resulting solution.

7. In the manufacture of stannous naphthenate from a water solution of an alkali metal naphthenate, the steps which comprise adding a water soluble stannous salt in solid form unmixed with water to cause a precipitation of stannous naphthenate, and separating the stannous naphthenate from the resulting solution.

8. The method of claim 7 in which the added water soluble stannous salt is stannous chloride.

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