EXHIBIT 14
UNITED STATES PATENT OFFICE

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AMINOMETHYLENEPHOSPHINIC ACIDS, SALTS THEREOF, AND PROCESS FOR THEIR PRODUCTION

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The present invention relates to aminomethylene-phosphinic acids, salts thereof, and the process of producing such compounds by reacting chloromethylphosphinic acid, or salts thereof, with ammonia, organic primary and secondary amines in the presence of a base.

The aminomethylene phosphinic acid compounds have the general formula:

\[
\begin{align*}
\text{R} \quad \text{N} \quad \text{O} \\
\text{R} \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{H} \quad \text{P} \quad \text{O} \\
\text{OM} \\
\text{OM} \\
\text{OM} \\
\end{align*}
\]

wherein R is from the group consisting of hydrogen, alkyl, aryl, alkyaryl, hydroxyalkyl, and

\[
\begin{align*}
\text{R} \quad \text{N} \quad \text{O} \\
\text{R} \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{H} \quad \text{P} \quad \text{O} \\
\text{OM} \\
\text{OM} \\
\text{OM} \\
\end{align*}
\]

radicals, \( R' \) is from the group consisting of \( R \), alkylene-N

\[
\begin{align*}
\text{R} \quad \text{N} \quad \text{O} \\
\text{R} \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{H} \quad \text{P} \quad \text{O} \\
\text{OM} \\
\text{OM} \\
\text{OM} \\
\end{align*}
\]

NRR', arylen-NRR', and heterocyclic alkylene-NRR' radicals, and M represents hydrogen and salt-forming cations.

The new compounds have a wide variety of uses such as chelating agents, wetting agents, biologically active compounds and as chemical intermediates for the production of aminomethylene phosphonic acids and derivatives thereof.

In the process of producing the new compounds, the first step is to neutralize the chloromethylphosphinic acid with the appropriate amine or metal bases to form the salts and then react the salt with the appropriate amine in the presence of excess amine or other base. In general, the reaction may be carried out in one step by simply using sufficient amine or other base to form the salt and effect the reaction without initial separation of the salt. However, it is satisfactory and sometimes desirable to start with an amine or alkali base salt of chloromethylphosphinic acid and carry out the second stage reaction with the desired primary or secondary amine. With an easily volatile amine compound, such as ammonia which is capable of forming bis and tris-methylphosphinic type products, it is generally preferred to first prepare the aminomono-methylene phosphinic compound and then react this compound with additional amounts of the chloromethylphosphinic acid salts to form the bis and tris-methylene phosphinic derivatives.

The general reaction which takes place may be illustrated by the following selected typical equations:

\[
\begin{align*}
\text{R} \quad \text{H} + \text{RR'NH} + \text{M'O} & \rightarrow \\
\text{OM} \\
\text{OM} \\
\text{OM} \\
\text{OM} \\
\end{align*}
\]

The products of the above equations are the same as shown in the above product formula, and M and M' are the same or different salt-forming cations, and \( R' \) is an alkylene, aminyl, or cycloalkylene radical.

Typical organic amino compounds which we have found suitable for use in the process may be illustrated by the following general types:

Mono and dialkyl amines (1—18 C atoms)
Mono and diaryl amines
Alkylene di- and polyamines
Phenylene diamines
Heterocyclic primary and secondary amines
Substituted alkyl primary and secondary amines
Substituted aryl primary and secondary amines

It has now been found that the above type primary and secondary amines readily react with chloromethylphosphinic acid and salts in aqueous alkaline solutions with release of hydrochloric acid and the formation of the aminomethylene phosphonic acid derivatives. In carrying out the reaction sufficient alkalinity must be present to neutralize the acidity of the chloromethylphosphinic acid and absorb the hydrochloric acid liberated by the reaction. In general, an excess of the alkaline base may be employed to drive the reaction to completion. The base may be an excess of the amine with which the desired reaction is to be carried out, but preferably the alkalinity may be obtained by the use of cheaper alkalies such as caustic soda.

The chloromethylphosphinic acid starting material may be prepared in accordance with the method described in U.S. patent application (Serial No. 65,018, filed Oct. 26, 1960) which comprises hydrolyzing chloromethylphosphonous chloride with water and removing the by-product, HCl, by vacuum.