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3,787,540

## BENZYLATION OF DIALKYL PHOSPHITES WITH DITHIOURETHANES

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6,972/71

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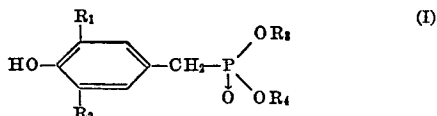
U.S. Cl. 260—970

10 Claims

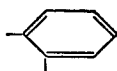
### ABSTRACT OF THE DISCLOSURE

Esters of p-hydroxybenzylphosphonic acids are prepared by reacting p-hydroxybenzylthiourethanes with esters of phosphonic acids in the presence of a base. The esters of p-hydroxybenzylphosphonic acids are stabilizers for polymers.

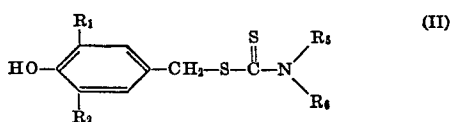
The present invention relates to a process for the manufacture of compounds of the Formula I



wherein  $\text{R}_1$  and  $\text{R}_2$  independently of one another denote a straight-chain or branched alkyl group, a cycloalkyl group or an aralkyl group, and  $\text{R}_3$  and  $\text{R}_4$  independently of one another denote a straight-chain or branched alkyl group, a cycloalkyl group, an alkylthioalkyl group, an alkoxalkyl group, a halogenoalkyl group, an alkenyl group, the phenyl group or an alkylphenyl group or together denote the groups  $-\text{CH}_2\text{CH}_2-$  or



characterized in that 1 mol of a compound of the Formula II



wherein  $\text{R}_1$  and  $\text{R}_2$  have the abovementioned meaning and  $\text{R}_3$  and  $\text{R}_4$  independently of one another denote a straight-chain or branched alkyl group or together, with inclusion of the nitrogen atom, denote a saturated heterocyclic ring, is reacted with one mol of a compound of the Formula III



wherein  $\text{R}_3$  and  $\text{R}_4$  have the abovementioned meaning, in the presence of a base.

It is known to manufacture p-hydroxybenzylphosphonates by reaction of appropriately substituted benzyl halides with trialkyl phosphites in the sense of an Arbusow reaction. In this, one alkyl group of the phosphite is split off as alkyl halide. The removal of the alkyl halide which has been split off from the end product frequently presents difficulties, especially if a higher alkyl halide such as, for example, octadecyl chloride, is concerned.

Against this, the process according to the invention avoids the formation of alkyl halide during the reaction, and this substantially facilitates the purification of the end product. Furthermore, the process according to the invention is economically advantageous because the dialkyl phosphite used, of the Formula III, is practically

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completely incorporated into the end product of the Formula I, whilst according to the previously known process a part of the trialkyl phosphite is lost in the form of the alkyl halide. The fact that the splitting off of alkyl halide is avoided in the process according to the invention also denotes a technological advance inasmuch as alkyl halides, especially lower alkyl halides, must be destroyed by combustion, and this requires expensive absorption installations to avoid contamination of the atmosphere, because of the halogen content. Finally, the substituted benzyl halides required for the previously known manufacturing process are unstable compounds of poor storage life, whilst the starting products of the Formula II required for the process according to the invention are stable compounds which can be stored.

It is furthermore known to manufacture compounds of the Formula I by reaction of appropriately substituted benzyl alcohols with trialkyl phosphites or triaryl phosphites, whilst splitting off alcohols or phenols. However, the benzyl alcohols required for this purpose are technically not as easily accessible as the starting products of the Formula II required for the process according to the invention. Additionally, what has been stated above applies as regards the more advantageous use of dialkyl phosphites according to the process of the invention.

Finally it is known to manufacture compounds of the Formula I by reaction of appropriately substituted benzyl-trialkyl-ammonium iodides with trialkyl phosphites in the sense of a modified Arbusow reaction. However, the manufacture of the benzyl-trialkyl-ammonium iodides requires a further process stage as compared to the starting products of the Formula II which can be used in accordance with the invention. Furthermore, this process suffers from the same disadvantages as the Arbusow reaction of benzyl halides with trialkyl phosphites, described above.

Further general advantages of the process according to the invention are the relatively low reaction temperatures and the short reaction times, which represses the undesired formation of colored by-products. The N,N-dialkyl-dithiocarbamates which are split off during the reaction can easily be separated off in the form of their water-soluble salts. These splitting products can therefore be isolated and again employed for the manufacture of the starting products of the Formula II, and this represents a further technical advantage. Furthermore, the dialkyl phosphites used in the process according to the invention are substantially less volatile when compared to the corresponding trialkyl phosphites hitherto used, and therefore cause distinctly less objectionable odor during the reaction.

According to the invention, compounds of the Formula I in which  $\text{R}_1$  and  $\text{R}_2$  independently of one another denote a straight-chain or branched alkyl group with 1 to 8 carbon atoms or a cycloalkyl group with 6 to 8 carbon atoms and  $\text{R}_3$  and  $\text{R}_4$  independently of one another denote a straight-chain or branched alkyl group with 1-22 carbon atoms, the groups  $-(\text{CH}_2)_{2-12}-\text{S}-\text{alkyl}$  or  $-(\text{CH}_2)_{2-12}-\text{O}-\text{alkyl}$ ,

wherein the alkyl groups possess 1-8 carbon atoms, an alkenyl group with 3 or 4 carbon atoms or the phenyl group, are preferentially manufactured.

In the preferred embodiment of the processes according to the invention, compounds of the Formula II are used in which  $\text{R}_3$  and  $\text{R}_4$  independently of one another denote a straight-chain or branched alkyl group with 1 to 5 carbon atoms or together, with inclusion of the nitrogen atom, form a hydrogenated heterocyclic 5-membered or 6-membered ring.

Particularly preferentially, compounds of the Formula I in which  $\text{R}_1$  denotes methyl or branched alkyl with 3-4 carbon atoms,  $\text{R}_2$  denotes branched alkyl with 3 or

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4 carbon atoms and  $R_3$  and  $R_4$  denote straight-chain or branched alkyl groups with 1-22 carbon atoms, propenyl, a  $-C_2H_4-S-$ alkyl group with 14-20 carbon atoms or phenyl, are manufactured according to the invention. Particularly preferentially, compounds of the Formula II in which  $R_5$  and  $R_6$  denote methyl, ethyl or propyl or together denote the radical of piperidine are employed for the manufacture of the compounds of the Formula I.

If  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  represent alkyl groups, these can, within the framework of the indicated limits, be methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, tert. butyl, amyl, tert.amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl or docosyl. These groups can also be present as alkyl substituents if  $R_3$  and  $R_4$  denote alkylphenyl. If  $R_3$  and  $R_4$  are halogenoalkyl groups, they can be 2-chloroethyl.  $R_1$  and  $R_2$  can also be cyclic alkyl groups with 6 to 8 carbon atoms. These can be, for example, cyclohexyl or cyclo-octyl; the preferred cyclic alkyl group is the 1-methylcyclohexyl-(1) group.  $R_1$  and  $R_2$  as aralkyl groups can, for example, denote benzyl or  $\alpha$ -phenyl-ethyl. If  $R_5$  and  $R_6$ , with inclusion of the nitrogen atom, form a heterocyclic 5-membered or 6-membered ring, this can be, for example, the radical of morpholine or piperidine.

If  $R_3$  is alkylthioalkyl, it can be hexadecylthioethyl, dodecylthioethyl, octylthioethyl, hexylthioethyl, ethylthioethyl, octadecylthiopropyl, dodecylthiopropyl or hexylthiopropyl. If  $R_3$  denotes alkylalkoxyalkyl, it can be dodecyloxyethyl or octadecyloxyethyl.  $R_3$  as alkenyl is, for example, allyl.

The solvents used in the process according to the invention are, for example, aromatic hydrocarbons such as benzene or toluene, higher-boiling ethers, such as dioxane or ethylene glycol dimethyl ether, aliphatic hydrocarbons, or hydrocarbon mixtures such as ligroin. Preferred solvents are ligroin and toluene. Bases used in the process according to the invention are, for example, alkali amides, such as  $LiNH_2$  and  $NaNH_2$ , and alcoholates such as  $NaOCH_3$ ,  $NaOC_2H_5$  and  $Mg(OC_2H_5)_2$ . Alkali amides are preferred.

Examples of compounds of the Formula III are dimethyl, diethyl, dibutyl, dihexyl, di-2-ethylhexyl, dioctyl, didodecyl, dihexadecyl, dioctadecyl, didocosyl, diphenyl or di-p-octylphenyl phosphite. The starting compounds of the Formula II can be manufactured from the corresponding 2,6-dialkylphenol, formaldehyde, carbon disulphide and a secondary amine, as described, for example, in U.S. Pat. 2,757,174.

In the process according to the invention, the reactants of the Formulas II and III are advantageously employed in molar ratios. If desired, one of the two reactants can be used in up to 20% excess. The base is employed in molar amounts relative to the Compound III.

The temperatures in the process according to the invention are not critical. They are only important for the speed at which the reaction takes place. If, for example, the process is carried out at 70° C., the reaction time is between 60 minutes and a few hours. Preferred temperature ranges are 40-100° C.

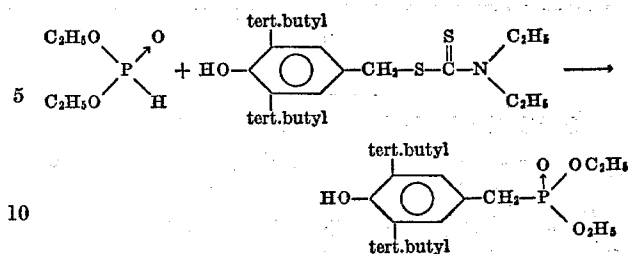
The reaction according to the invention is preferably carried out whilst passing nitrogen or a noble gas through the mixture. The reaction according to the invention can for example be carried out by adding the base to a solution of the Compound III and then adding the Compound II in the same solvent as the Compound III, at elevated temperature.

The compounds obtained in accordance with the process of the invention are outstandingly suitable for use as stabilizers against the thermo-oxidative and/or light-induced degradation of monomeric and polymeric substances, especially for the stabilisation of polypropylene, polyethylene, polyamides, polyurethanes, polyacetals or copolymers of ethylene, propylene and a diene such as, for example, norbornadiene or dicyclopentadiene.

The invention is explained in more detail in the examples which follow.

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## EXAMPLE 1



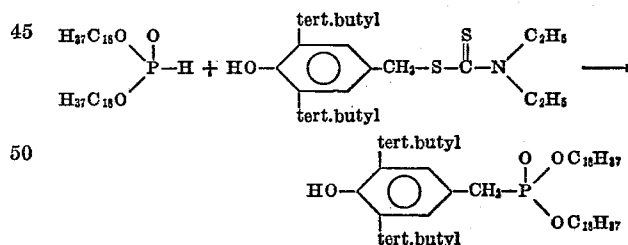
15 13.8 g. (0.1 mol) of diethyl phosphite are dissolved in 50 ml. of ligroin and 3.9 g. (0.1 mol) of sodium amide are added. 36.8 g. (0.1 mol) of N,N-diethyl-dithiocarbamic acid 3,5-ditert.butyl-4-hydroxybenzyl ester, dissolved in 120 ml. of hot ligroin, are added dropwise at 60° C. The mixture is kept for 3 hours at 70° C. and is then cooled to room temperature, and 200 ml. of toluene are added. The toluene solution is repeatedly washed with water and evaporated. The residue is recrystallized from ligroin. 27 g. (75%) of 4-hydroxy-3,5-ditert.butylbenzylphosphonic acid dialkyl ester of melting point 122° C. are thus obtained.

25 If, in this example, the diethyl phosphite is replaced by an equimolecular amount of one of the dialkyl phosphites of the Table 1 below and otherwise the same procedure is followed, the 4-hydroxy-3,5-ditert.butylbenzylphosphonic acid dialkyl esters having the indicated physical data are obtained.

TABLE 1

Dialkyl phosphite	Data of the resulting 4-hydroxy-3,5-ditert.butylbenzylphosphonic acid dialkyl ester
$(\text{CH}_3)_2\text{PHO}$ .....	Melting point, 155-157° C.
$(\text{C}_2\text{H}_5)_2\text{PHO}$ .....	Melting point, 45-48° C. Boiling point, 180-184° C./0.2 mm. Hg.
$(\text{CH}_3=\text{CH}-\text{CH}_2\text{O})_2\text{PHO}$ ....	Boiling point, 160-165° C./0.1 mm. Hg.

## EXAMPLE 2



55 29.3 g. (0.05 mol) of dioctadecyl phosphite are dissolved in 100 ml. of ligroin and a suspension of 1.2 g. of sodium methylate in 20 ml. of ligroin is added at 20° C. Thereafter the mixture is heated to 60° C. and a solution of 18.38 g. (0.05 mol) of N,N-diethyl-dithiocarbamic acid 3,5-ditert.butylhydroxybenzyl ester in 70 ml. of toluene is added dropwise. The mixture is now heated for 3 hours at 72° C. and a further 1½ hours under reflux. After cooling, undissolved matter is filtered off and the filtrate is concentrated to dryness in vacuo. The residue is chromatographed on silica gel G, using a mixture of 95% of toluene and 5% of methanol as the eluting agent. The eluates are evaporated and the product is recrystallized from acetone. 4-hydroxy-3,5-ditert.butylbenzylphosphonic acid dioctadecyl ester of melting point 57° C. is thus obtained.

70 If in this example the dioctadecyl phosphite is replaced by an equimolecular amount of one of the phosphorous acid diesters of Table 2 below and otherwise the same procedure is followed, the 4-hydroxy-3,5-ditert.butylben-

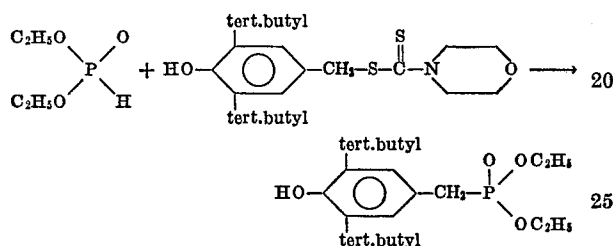
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zyl-phosphonic acid diesters having the indicated physical data are obtained:

TABLE 2

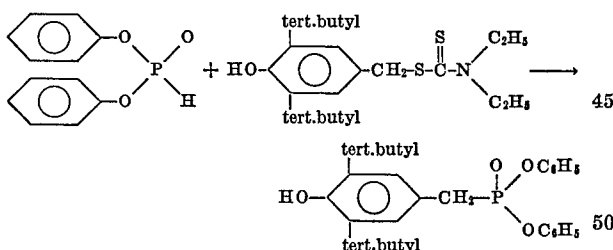
Phosphite	Data of the resulting 4-hydroxy-3,5-ditertbutylbenzyl-phosphonic acid diester
$(\text{H}_{25}\text{C}_{15}\text{O})_2\text{PHO}$	Light yellow oil.
$(\text{H}_{17}\text{C}_8-\text{C}(\text{CH}_3)_2-\text{CH}_2\text{O})_2\text{PHO}$	Do.
$(\text{H}_{33}\text{C}_{18}\text{O})_2\text{PHO}$	Melting point, 44-46° C.
$(\text{H}_{45}\text{C}_{22}\text{O})_2\text{PHO}$	Melting point, 45-48° C.
$(\text{H}_{25}\text{C}_{15}\text{SCH}_2\text{CH}_2\text{O})_2\text{PHO}$	Light yellow oil.
$(\text{H}_{37}\text{C}_{18}\text{SCH}_2\text{CH}_2\text{O})_2\text{PHO}$	Melting point, 50° C.

## EXAMPLE 3



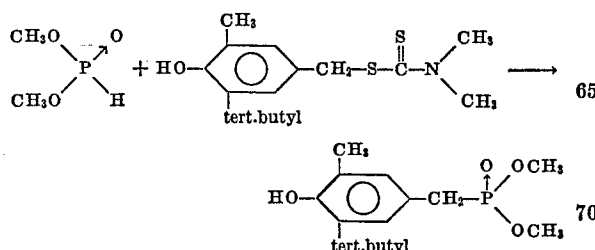
13.8 g. (0.1 mol) of diethyl phosphite are dissolved in 50 ml. of ligroin and 3.9 g. (0.1 mol) of sodium amide are added. 38.2 g. (0.1 mol) of morpholyl-dithiocarbamic acid 3,5-ditert.butyl-4-hydroxybenzyl ester, dissolved in 120 ml. of ligroin, are added dropwise at 60° C. The mixture is kept for 3 hours at 80° C., 200 ml. of toluene are added and the whole is cooled. The organic phase is repeatedly washed with water, dried and evaporated. The solid which remains is recrystallized from ligroin. 4-hydroxy-3,5-ditert.butylbenzyl-phosphonic acid diethyl ester of melting point 122° C. is thus obtained in a yield of 81%.

## EXAMPLE 4



The procedure of Example 1 is repeated, the diethyl phosphite being replaced by an equimolecular amount of diphenyl phosphite or di-(p-tert.octylphenyl)-phosphite. The 4-hydroxy-3,5-ditert.butylbenzyl-phosphonic acid diphenyl ester obtained in a yield of 73% if the same procedure is followed melts at 135° C., whilst the 4-hydroxy-3,5-ditert.butylbenzyl-phosphonic acid di-(p-tert.octylphenyl) ester is a light yellow glass.

## EXAMPLE 5



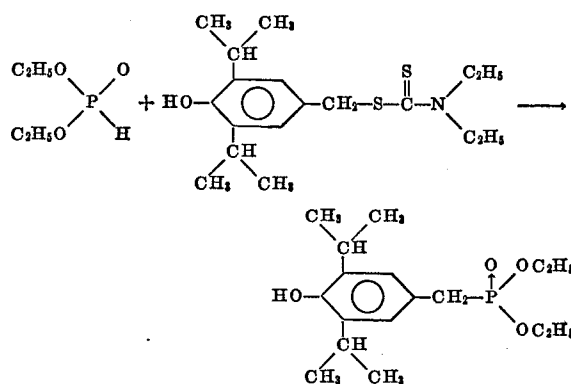
11.0 g. (0.1 mol) of dimethyl phosphite are dissolved in 50 ml. of toluene and 2.3 g. (0.1 mol) of lithium amide are added. A solution of 26.5 g. (0.1 mol) of N,N-

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dimethyl-dithiocarbamic acid 3-methyl-4-hydroxy-5-tert.butylbenzyl ester in 100 ml. of toluene is added dropwise at 60° C. The mixture is kept for 3 hours at 80° C. and is then cooled to room temperature and filtered. The filtrate is repeatedly washed with water, dried and evaporated. The residue is recrystallized from ligroin. 23 g. (81%) of 3-methyl-4-hydroxy-5-tert.butylbenzyl-phosphonic acid dimethyl ester of melting point 102° C. are thus obtained.

If in this example the dimethyl phosphite is replaced by an equivalent amount of diethyl phosphite and otherwise the same procedure is followed, 3-methyl-4-hydroxy-5-tert.butylbenzyl-phosphonic acid diethyl ester is obtained in a yield of 75% of theory, and with a melting point of 102° C.

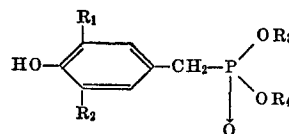
## EXAMPLE 6



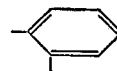
13.8 g. (0.1 mol) of diethyl phosphite are dissolved in 50 ml. of ligroin and 3.9 g. (0.1 mol) of sodium amide were added. 34.0 g. (0.1 mol) of N,N-diethyl-dithiocarbamic acid 3,5-diisopropyl-4-hydroxybenzyl ester, dissolved in 100 ml. of hot ligroin, are added dropwise at 60° C. The mixture is kept for 3 hours at 70° C. and is then cooled to room temperature and filtered. The filtrate is repeatedly washed with water and evaporated, and the oily residue is distilled in a high vacuum. 4-hydroxy-3,5-diisopropylbenzyl-phosphonic acid diethyl ester is obtained as a colorless oil of boiling point 162-164° C./0.15 mm. Hg.

We claim:

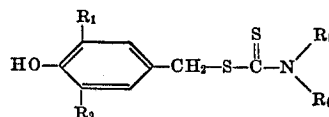
1. Process for the manufacture of compounds of the formula



wherein  $\text{R}_1$  and  $\text{R}_2$  independently of one another are a straight-chain or branched alkyl group, a cycloalkyl group or an aralkyl group, and  $\text{R}_3$  and  $\text{R}_4$  independently of one another are a straight-chain or branched alkyl group, a cycloalkyl group, an alkylthioalkyl group, an alkyloxalkyl group, a halogenoalkyl group, an alkenyl group, the phenyl group or an alkylphenyl group or together are the groups  $-\text{CH}_2\text{CH}_2-$  or



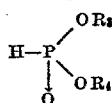
wherein 1 mol of a compound of the formula



wherein  $\text{R}_1$  and  $\text{R}_2$  are as defined above and  $\text{R}_5$  and  $\text{R}_6$  independently of one another are a straight-chain or branched alkyl group or together, with inclusion of the

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nitrogen atom, are a saturated heterocyclic ring, is reacted with one mol of a compound of the formula



wherein  $R_3$  and  $R_4$  are as defined above, in the presence of a base.

2. Process according to claim 1, wherein lithium amide is used as the base.

3. Process according to claim 1, wherein sodium amide is used as the base.

4. Process according to claim 1, wherein sodium methylate is used as the base.

5. Process according to claim 1, wherein the reaction is carried out in the presence of molar amounts of a base.

6. Process according to claim 1, wherein  $R_1$  and  $R_2$  independently of one another are a straight-chain or branched alkyl group with 1 to 8 carbon atoms or a cycloalkyl group with 6 to 8 carbon atoms and  $R_3$  and  $R_4$  independently of one another are a straight-chain or branched alkyl group with 1-22 carbon atoms, the  $-(\text{CH}_2)_{2-12}-\text{S}-\text{alkyl}$  or  $-(\text{CH}_2)_{2-12}-\text{O}-\text{alkyl}$  groups, wherein the alkyl groups possess 1-8 carbon atoms, an alkenyl group with 3 or 4 carbon atoms or the phenyl group.

7. Process according to claim 1, wherein  $R_1$  and  $R_2$  independently of one another are a straight-chain or branched alkyl group with 1 to 8 carbon atoms or a cycloalkyl group with 6 to 8 carbon atoms and  $R_3$  and  $R_4$

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independently of one another are a straight-chain or branched alkyl group with 1-22 carbon atoms or the  $-(\text{CH}_2)_{2-12}-\text{S}-\text{alkyl}$  or  $-(\text{CH}_2)_{2-12}-\text{O}-\text{alkyl}$  groups, wherein the alkyl groups possess 1-8 carbon atoms.

8. Process according to claim 1, wherein  $R_5$  and  $R_6$  independently of one another are alkyl with 1-5 carbon atoms or together, with inclusion of the nitrogen atom, form a hydrogenated heterocyclic 5-membered or 6-membered ring.

9. Process according to claim 6, wherein  $R_1$  is methyl or branched alkyl with 3-4 carbon atoms,  $R_2$  is branched alkyl with 3 or 4 carbon atoms and  $R_3$  and  $R_4$  are straight-chain or branched alkyl groups with 1-22 carbon atoms, propenyl, a  $-\text{C}_2\text{H}_4\text{S}-\text{alkyl}$  group with 14-20 carbon atoms or phenyl.

10. Process according to claim 7, wherein  $R_5$  and  $R_6$  are methyl, ethyl, propyl, isopropyl or together are the radical of piperidine.

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LEWIS GOTT, Primary Examiner

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U.S. Cl. X.R.

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