

[54] **INHIBITORS FOR OLEFIN COMPLEXING PROCESS**

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[58] Field of Search **260/677 A, 683.15, 260/681.5 C, 666.5**

[56] **References Cited**

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[57] ABSTRACT

Combinations of organic phosphines and organic nitrogen bases help stabilize complexing solutions containing cuprous and silver salts whose anionic components are Lewis acids, said salts being dissolved in aromatic solvents, when the solutions are in the presence of olefins, to prevent side reactions from occurring during olefin complexing processes in which the above complexing solutions are employed.

11 Claims, No Drawings

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DESCRIPTION OF THE PRIOR ART

It is known in the art to use various copper and silver salts whose anionic components are Lewis acids such as CuPF_6 , CuBF_4 , CuAlCl_4 and the like and corresponding silver salts as complexing agents.

However, the use of these salts, when dissolved in aromatic hydrocarbon solvents, in olefin complexing processes have serious drawbacks making their use less practicable. It is known that these types of materials tend to dissociate in solution yielding Lewis acid moieties such as AlCl_3 and the like. These Lewis acids when in the presence of small amounts of HCl and other proton donor materials are known to catalyze alkylation of the aromatics by the olefins and other side reactions leading to the inactivation of the complex. Hence, the need to minimize or eliminate these alkylation and side reactions is suitably desired by the art.

SUMMARY OF THE INVENTION

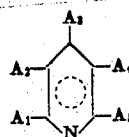
In accordance with the present invention, the addition of minor amounts of phosphines, in combination with minor amounts of organic nitrogen bases to aromatic solutions containing complexing materials such as CuPF_6 , CuBF_4 , CuBF_3Cl , CuAlCl_4 , CuAlBr_4 , CuTaF_6 , CuAlCl_2Br , and the like and their corresponding silver salts, said solutions being used in an olefin complexing process, provides increased stability for said solutions and substantially prevents alkylation of the aromatic by the olefin and olefin polymerization side reactions.

The use of CuAlCl_4 , CuBF_4 and the like, dissolved in suitable solvents such as aromatic hydrocarbons in olefin separation-by-complexing processes has associated problems which makes their use less practical in a commercial olefin recovery process. It is known that these particular cuprous salts, and equally the corresponding silver salts, dissociate somewhat in solution to yield Lewis acid materials such as AlCl_3 and BF_3 . These Lewis acid materials, when in the presence of proton donors such as HCl , catalyze alkylation of aromatics by olefins and at high pressures cause olefin polymerization to occur. Hence, in an olefin complexing process, where the above-described cuprous and silver salts are being employed in aromatic solvent materials, alkylation and polymerization side reactions can be expected to occur.

It has been unexpectedly discovered that the rate of alkylation in the above-described systems can be substantially reduced by adding to the complexing solutions, in effective amounts, phosphine materials in combination with organic nitrogen base compounds. It is believed that the alkylation rates may be reduced in the above manner because of the neutralization of the proton donor material, which is typically HCl , and that such neutralization by the organic nitrogen bases can occur even in the presence of the Lewis acid moieties such as AlCl_3 , BF_3 and the like. The addition of the phosphine material is believed to add stability to the overall system and allow this neutralization to occur and thereby provide long range stability for the system at a better level than the organic nitrogen additive alone.

The phosphine materials which are useful in the present invention include moieties such as trialkyl phosphines, alkylaryl phosphines, aralkyl phosphines, benzyl phosphines and materials having the general formula $\text{R}_1\text{R}_2\text{R}_3\text{P}$ wherein R_1 , R_2 and R_3 are monovalent radicals independently selected from the group consisting of alkyl radicals having from one to 20 carbon atoms, preferably from two to 10 carbon atoms; phenyl radicals, alkylaryl radicals having from seven to 12 carbon atoms; preferably from seven to 10 carbon atoms; aralkyl radicals having from seven to 12 carbon atoms, preferably from seven to 10 carbon atoms.

Representative non-limiting examples of useful phosphine materials include triphenyl phosphine, trioctyl phosphine, tribenzyl phosphine and tritolyl phosphine. The organic nitrogen bases useful in the present invention are generally defined as aprotic and lack other polar functional groups, they include classes of compounds known as substituted pyridines, tertiary alkyl amines, and tertiary alkylaryl amines. By substituted pyridines is meant any alkylated pyridine having the general formula:



wherein A_1 - A_5 are monovalent radicals independently selected from the group consisting of hydrogen radicals and alkyl groups whose total number of carbon atoms ranges from one to 18. The term substituted pyridine includes moieties such as 2, 4, 6-trimethyl pyridine, 2,6-ditertiary butyl pyridine, 2-methyl pyridine and the like. By tertiary alkyl amines is meant compounds having the general formula, $\text{RR}'\text{R}''\text{N}$ wherein R , R' and R'' are independently selected from the group consisting of alkyl radicals having from one to 10 carbon atoms, preferably from one to five carbon atoms and having at least six carbon atoms per nitrogen; tertiary alkylaryl amines are materials represented by the general formula $\text{ArRR}'\text{N}$ wherein Ar is a substituted aryl group having at least six carbon atoms and R and R' have the above designated meanings.

Representative non-limiting examples of organic nitrogen base materials useful in this invention include α -picoline, β -picoline, γ -picoline; 2,6 and other lutidines, collidines symmetrical and unsymmetrical, ethyl and polyethyl pyridines, N-ethyl pyrrolidine, N-ethyl piperidine, tributyl amine, 2,6-diethyl N,N-diethyl aniline and the like.

The amounts of phosphine and organic nitrogen base additives have been described as minor amounts. By minor amounts is meant from 0.1 to 15 percent, preferably from 0.5 to 10 percent based on the number of moles of the complexing salt employed. Minor amounts of these additives are used to avoid excessive loss of complexing capacity of the complexing salt and moreover since minor amounts of said additives provide sufficient stability by lowering alkylation side reactions to a minimum.

The complexing solution may be generally described as low volatility aromatic solvents containing cuprous or silver complexing salts such as CuPF_6 , CuBF_4 , CuBF_3Cl , CuAlCl_4 , CuAlBr_4 , CuTaF_6 and CuAlCl_2Br , where $x + y = 4$. These complexing solutions are more adequately described and set forth in copending application Ser. No. 259,077, said application being incor-

porated herein by reference. Additionally the use of these complexing solutions in an olefin complexing process may be found in copending application Ser. No. 259,078, said application also incorporated herein by reference.

The temperatures and pressures at which the present invention is operable are not critical and generally will range from about 20° to 300°C., preferably from 50° to 140°C., and from 0.01 to 0.5 atmospheres to about 10 to 50 atmosphere pressure.

In a typical reaction scheme 4 mole % triphenyl phosphine and 7 mole % 2,4,6-collidine are employed in a solution of CuAlCl_4 in 2.5 moles of cumene. The solution absorbs ethylene reversibly from an ethylene containing feedstream while alkylation and other side reactions are minimized.

The present invention may be illustrated but is not necessarily limited by the following examples.

EXAMPLE I

55.0g of a CuAlCl_4 -methylbiphenyl-complex, 1.10g CuCl , 0.72g triphenylphosphine and 0.53 g 2,6-di-tert.-butylpyridine are heated to 140°C. under a nitrogen atmosphere in a reaction vessel equipped with magnetic stirrer, gas inlet and outlet. The input and output of gas are monitored by means of two gas meters. Ethylene is introduced through a tube ending shortly above the liquid level and a slow purge of gas is maintained to avoid vapor locking. After the initial uptake of ethylene due to complexing by the copper salt is complete, no further consumption of gas can be observed over a period of 4½ hours. An analogous run without the 2,6-di-tert.-butylpyridine showed continuous uptake of ethylene at a rate of 400 ml per hour per mole of copper. This shows that 2,6-di-tert.-butylpyridine is able to suppress the alkylation side reaction when used together with triphenylphosphine as additive.

EXAMPLE IIa

75.1g CuAlCl_4 -methylbiphenyl complex, 1.43g 2,6-di-tert.-butylpyridine and 1.97g triphenylphosphine were heated to 140°C. under ethylene atmosphere. After 360 hours during which no alkylation was observable, a continuous uptake of ethylene could be observed due to alkylation.

EXAMPLE IIb

75.1g CuAlCl_4 -methylbiphenyl complex and 1.43g 2,6-di-tert.-butylpyridine were heated to 140°C. under identical conditions as described in Example IIa, alkylation started after 232 hours.

Examples IIa and IIb clearly show that the combination of an organic phosphine and an organic nitrogen base is superior in terms of the duration of an olefin

separation process before alkylation begins. The inhibitor action is not due to the phosphine alone since previous determinations showed that phosphine by itself is not a satisfactory additive. For example, a solution of CuAlCl_4 in methylbiphenyl containing 1.83 mole % of triphenylphosphine consumed ethylene at 140°C. at a rate of 7.7 mole % per day for 47 hours at which point alkylation of the system began.

EXAMPLE III

In this example, the rate of alkylation was measured by saturating the complex with ethylene at atmospheric pressure and maintaining it under an ethylene atmosphere in a thermostated glass vessel connected to an oil-fitted "wet-test" meter, in such a way that any ethylene uptake following the initial saturation would be recorded in the meter. The alkylation rate was expressed as millimoles of ethylene per mole of CuAlCl_4 per hour.

In the first series of tests, runs in benzene at 50°C. the alkylation rate in the absence of any additive varied from 9 to 25 units. Certain additives reduced it slightly but substituted pyridine namely 2,6-di-tertiary butyl pyridine and collidine 2,4,6-trimethyl pyridine reduced it to immeasurably low values, below 0.02 units; the results of these runs are summarized in Table I below:

TABLE I

STABILITY RUNS IN BENZENE AT 50°C.

Additive	Concentration Mole % on CuAlCl_4	Alkylation Rate mmole C_2H_4 /mole CuAlCl_4 per hour	Time on Test Hours
None	0	25	2
		9	14
		25	13.5
Tributyl Stibine	1.57	7.8, 7.2	16.5
Triphenyl Phosphine	1.65	1.4	16
Triethyl Aluminum	0.95	0.9, 1.4	15.5, 5
Di- <i>t</i> -butyl pyridine	6.9	0.02	20
	7.6	0.1	15
Collidine	8.45	0.00	16
		0.00	21

EXAMPLE IV

The procedure of Example III was repeated with a number of high boiling solvents at temperatures of up to 140°C. Results of these runs are found summarized in Table II below and show that the additives of the present invention are equally effective even at the higher temperatures. Note that in the absence of any additive, alkylation rates of 18 and 46 units were obtained even at temperatures as low as 50°C. and 75°C. The addition of collidine, a representative nitrogen base reduced the alkylation rates to zero at temperatures up to 140°C. and at times up to 212 hours.

TABLE II.—STABILITY RUNS IN HIGH BOILING SOLVENTS

Solvent	Mole percent additive	Temp. °C.	Alkylation rate C_2H_4 / Cu/hr. $\times 10^3$	Time on test hrs.
Cumene.....	2.6 Al $\text{Et}_3 + \phi_3\text{P}$	98	1.5	15
Biphenyl + chlorobiphenyl.....	2.4 Al $\text{Bu}_3 + \phi_3\text{P}$	140	500	(1)
Diphenyl methane.....	2.4 Al Bu_3	138, 140	26, 47	5, 3
Methyl biphenyl.....	2.95 Al $\text{Bu}_3 + 1.83 \phi_3\text{P}$	140	3.0, 3.4	24, 23
3,3' dimethyl biphenyl.....	6.38 Al Et_3	120	3300	5
O-isopropyl biphenyl.....	2.5 Al Bu_3	140	0.3	22
Cumene.....	None.....	50, 75	18, 46	16, 44
Do.....	8.23 Collidine.....	100	0.00, 0.00	15, 45
Do.....	7.0 Collidine, 4.6 $\phi_3\text{P}$	100	0.02	66
Methyl biphenyl.....	2.8 Collidine.....	140	0.00	17
Do.....	6.6 Collidine.....	140	0.00	212
Do.....	4.5 Collidine + 4.4 Al ϕ_3	140	0.0	3

¹ Minutes.

NOTE.— Et_3 =Triethyl; Bu_3 =Tributyl; ϕ_3 =Triphenyl.

EXAMPLE V

In this example the solubility of pyridine — AlCl_3 complex is compared to that of collidine — AlCl_3 in benzene solutions. To separate CuAlCl_4 -benzene solutions was added sufficient amounts of pyridine and collidine respectively. The precipitates formed were analyzed for % Cu, Al, Cl and C; the results of these analyses are found below:

	Additive:	Pyridine	Collidine
% Cu		23.6	55.48
% Al		7.57	0.0
% Cl		47.8	42.2
% C		14.82	1.45
Ratio Nitrogen Base/Cu		0.67	0.02
Ratio Al/Cu		0.76	0.0

The above data indicate that pyridine causes sizable amounts of organic base to form in the precipitate and equal amounts of Al and organic base showing that the precipitate is $\text{CuCl} + \text{Base} : \text{AlCl}_3$ adduct. This in turn means that pyridine is ineffective as an inhibitor since it is removed from the aromatic solution and therefore cannot neutralize the HCl proton donor material. With collidine, little aluminum or base is present in the precipitate which is mostly CuCl with the $\text{Base} : \text{AlCl}_3$ adduct remaining in solution and able to react with HCl to thereby minimize alkylation of the solution.

What is claimed is:

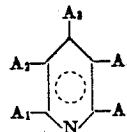
1. An improved process for the separation and recovery of complexible olefins from olefin-containing feedstreams by contacting said feedstreams with an aromatic sorbent solution containing cuprous salts whose anionic components are Lewis acids wherein the improvement comprises incorporating into said aromatic sorbent solution a minor amount of an organic phosphine in combination with an organic nitrogen base material selected from the group comprising alkyl amines, tertiary alkylaryl amines and substituted pyridines, to thereby substantially reduce alkylation and polymerization side reactions and stabilize said aromatic sorbent solution.

2. The process of claim 1 wherein said organic phosphine has the general formula $\text{R}_1\text{R}_2\text{R}_3\text{P}$ wherein R_1 , R_2 , and R_3 are monovalent radicals independently selected from the group consisting of alkyl radicals having from one to 20 carbon atoms, phenyl radicals, alkylaryl radicals having from seven to 12 carbon atoms and aralkyl radicals having from seven to 12 carbon atoms.

3. The process of claim 1 wherein said organic nitrogen base material is an alkyl amine having the general

formula: $\text{RR}'\text{R}''\text{N}$ wherein R, R', and R'' are independently selected from the group consisting of alkyl radicals having from one to 10 carbon atoms.

4. The process of claim 1 wherein said organic nitrogen base material is a substituted pyridine having the general formula:



wherein $\text{A}_1\text{--A}_5$ are monovalent radicals independently selected from the group consisting of hydrogen radicals and alkyl groups whose total number of carbon atoms ranges from one to 18.

5. The process of claim 1 wherein said organic nitrogen base material is a tertiary alkylaryl amine having the general formula $\text{ArRR}'\text{N}$ wherein Ar is a substituted aryl group having at least six carbon atoms; R, and R' are independently selected from the group consisting of alkyl radicals having from one to 10 carbon atoms.

6. The process of claim 1 wherein from 0.1 to 15 percent of said organic phosphine and organic nitrogen base material, based on number of moles of complexing salt, is present in said aromatic sorbent solution.

7. The process of claim 1 wherein said complexible olefins to be recovered are ethylene and propylene.

8. The process of claim 1 wherein said contacting is carried out at temperatures in the range of from about 20° to 300°C . and pressures ranging from 0.5 to about 50 atm.

9. The process of claim 1 wherein said cuprous salt is one selected from the group consisting of CuPF_6 , CuBF_4 , CuBF_3Cl , CuAlCl_4 , CuAlBr_4 , CuTaF_6 and $\text{CuAlCl}_2\text{Br}_x$ wherein $x + y$ are integers whose sum equals 4.

10. The process of claim 1 wherein said organic nitrogen base is one selected from the group consisting of 2,4,6-trimethyl pyridine, 2,6-ditertiary butyl pyridine, 2,6-diethyl N,N-diethyl aniline and tributyl amine.

11. The process of claim 1 wherein said organic phosphine is one selected from the group consisting of triphenylphosphine, trioctylphosphine, tribenzylphosphine and tritolyphosphine.

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