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(54) CONTROLLED SCRUBBING OF EFFLUENT GASES CONTAINING WASTE HALIDES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for removing halide vapour from a waste gas.

The commercial production of metallic or non-metallic halides (such as $TiCl_4$) often results in a waste gas which contains small amounts of waste halides in a gaseous state. The waste gas can be predominately a purge gas, such as CO, CO_2, N_2, halogen, and acid halide, Disposal of the waste gas by venting directly to the atmosphere, even after conventional scrubbing (water-dilute acid scrubbing) results in an optically dense cloud (often referred to as a plume) thought to be caused by hydrolysis of the small amount of waste halides present. Thus, it is aesthetically desirable to have essentially complete removal of the small amount of waste halides prior to venting the waste gas into the atmosphere.

The invention provides a process for removing halide vapour from a waste gas which process comprises (A) generating an absorptive aqueous mist containing water in which is dissolved one or more of HCl HNO_3, HBr, HF and HI and/or one of more halide salts of the following carbons, namely calcium, sodium, ammonium, lithium, barium and iron; (B) bringing the waste gas into contact with the absorptive aqueous mist; the temperature of the combined waste gas stream and absorptive aqueous mist being maintained at from −5°C to 70°C., the water vapour pressure of the absorptive aqueous mist being maintained at from 0.05—5 mm Hg prior to and during the contact and the particle size of the aqueous absorptive mist being such that the ratio of the surface area of the absorptive aqueous mist to the weight of the halide to be removed is at least two square meters surface area of the absorptive aqueous mist per gram of halide; and (C) effecting additional processing to remove mist from the gas/mist mixture and to remove halide acid from the gas.

The process of the present invention is employed to cleanse waste halides (e.g., $TiCl_4$) from a waste gas stream containing waste halide impurities. As indicated earlier, the presence of even small amounts of wate halides in waste gas streams results in the formation of highly visible clouds, known as plumes, when the waste gas stream is brought into contact with the atmosphere. It is postulated that these plumes form because hydrolysis occurs when the waste halides are contacted with water vapor either through the atmosphere or by conventional scrubbing (e.g., water-dilute acid scrubbing). For example, when a $TiCl_4$-containing gas stream is vented to the atmosphere or conventionally scrubbed, it appears as dense white clouds upon exit from the stack. Formation of these clouds is aesthetically undesirable, and it is in the interest of a cleaner environment that they be eliminated. The process of the present invention in particular enables the removal of titanium tetrachloride and other waste halide impurities from waste gas streams containing these impurities, with the result that the waste gas streams emitted to the atmosphere are devoid of such impurities and therefore do not appear as optically dense clouds.

In the process of the present invention, a waste gas stream containing waste halide impurities is contacted with an aqueous acid mist containing HCl, HNO_3, HBr, HF, and HI, or a halide salt of calcium, sodium, ammonium, lithium, barium, and iron. The mist can be liquid droplets of about 5000 microns or less dispersed in a gas. The mist can be produced by the use of apparatuses such as a baffle column, an orifice scrubber, a spray tower, or an atomizer. When the waste gas stream and absorptive aqueous mist are contacted, the waste halide impurities present in the waste gas stream are rapidly absorbed into the mist. Contact between the gas stream and the mist may be cocurrent or countercurrent.

The ratio between surface area of the aqueous mist and the weight of the waste halide impurities is at least 2 square meters surface area of mist per gram of waste halide impurity present in the waste gas. The preferred ratio is about 12—16 square meters surface area mist per gram of waste halide impurity. This range is preferred because it provides optimum contact between the waste gas and the mist, thereby maximizing absorption of the waste halide into the mist and minimizing hydrolysis. Although the ratio can be as high as 50, so much energy is required to attain this ratio that operation at such a high ratio is not economical. The surface area of the mist is defined as the surface area of each particle (e.g., if each particle is spherical then the surface area is 4π times the radius squared of an average sized particle) multiplied by the number of particles generated, which surface area can be easily calculated for each specific piece of equipment. The amount of halide gas in the waste gas can be calculated by using Rault's Law, as described in Perry et al., *Chemical Engineers' Handbook,* McGraw Hill, New York, N.Y. (1963) pages 4—59.

After the waste halide impurities are absorbed into the mist, the gas can be separated from the mist by passing a stream of the residual gas mixed with the mist through a conventional gas-liquid separator such as a conical separator. The mist containing waste halide impurities, can be collected as a liquid, and if the collected liquid contains an acid, the acid can be recovered by distillation and reused in the process of the present invention or, if one does not wish to distill and reuse the acid, it can be neutralized to its corresponding salt and disposed of as waste; similarly if the liquid collected contains only waste halide salts it can be disposed of as waste.

In order to remove vaporous halide acid which is formed during formation of the waste gas, scrubbing with water may, for example, be effected. The halide acid present will be the acid of a halide present in the waste gas (e.g., if a metal chloride is being produced, then the waste gas contains, as acid, HCl). The vaporous halide acid is removed because of its corrosive nature. The halide acid so removed (especially when in aqueous form) can then be used in the process of the present invention. The residue of the waste gas will be composed predominantly of inert gases and can be vented to the atmosphere without producing an objectionable plume.

Waste halides which can be cleansed from a waste gas stream by the process of the present invention include the halides of titanium, aluminum, vanadium, silicon, tin, magnesium, zinc, antimony, sulfur, phosphorus and ammonium. The amount of halide impurities which can be present in the waste gas stream is from trace amounts to about 10 weight percent based on the total weight of the waste gas. Of the various herinbefore specified acids which can be used in the process of the present invention, an acid which contains the same halide anion as the impurity that is to be removed from the waste gas has been found to provide best results. For instance, if one wanted to remove a chloride impurity, then one would choose HCl because both the impurity and the acid contain the chloride anion. The most preferred acid will normally be HCl for an additional reason, namely that when it is neutralized with a base (e.g. NaOH or $Ca(OH)_2$) it forms chloride salts (e.g. NaCl or $CaCl_2$) which are more easily disposable than the salts formed by the other acids.

Of the various hereinbefore specified halide salts which can be used in the process of the present invention, a salt which contains the same halide group as the impurity that is to be cleansed from the waste gas has been found to give best results. Thus, for removing chloride impurities, a chloride salt such as sodium chloride will be preferred. Sodium chloride is preferred for another reason: that of its economy and disposability.

The concentration of acid required is dependent upon the type of acid used and the temperature. The process is normally operated at low pressure (e.g., about 4 psig). Under normal operating conditions for the production of waste halides, the initial temperature of the waste gas is −30 to 20°C. The concentration and initial temperature of the mist can be adjusted so that the combined waste gas stream and mist has the required temperature within the earlier specified range from −5 to 70°C., and the water vapor pressure of the mist both before and during contact with the waste gas is 0.05—5 mm Hg. Water vapor pressure for each mist varies with concentration and temperature. Specific concentrations and temperatures to obtain the vapor pressures of the aqueous acid or aqueous waste halide mists used in the practice of the present invention can be determined by referring to Perry et al., *Chemical Engineers' Handbook,* McGraw Hill, New York, N.Y. (1963), pages 3—60 to 3—64 and 3—227 and 3—228, and Chu et al., *Vapor-Liquid Equilibrium Data,* J. W. Edwards, Ann Arbor, Michigan (1956). The preferred water vapor pressure of the mist is as low as possible because this minimizes the vapor phase hydrolysis of the metal halides.

The preferred temperature of the waste gas stream is about −15 to −30°C. because at these temperatures most of the waste halides are condensed out and the waste gas stream contains the least amount of waste halides. This means less mist is required to scrub the waste halides.

The following examples are illustrative of the invention. All parts, percentages, and proportions are by weight unless otherwise indicated.

EXAMPLE 1.

Dried gas at 15°C., composed essentially of nitrogen, and about 2.6 weight percent $TiCl_4$ is contacted with 29 weight percent aqueous HCl mist containing 1.9 weight percent titanium in a 2.5 inch (outside diameter) glass baffle column which is 11 inches in length and contains 20 trays. The HCl is introduced into the column through a ¼″ diameter glass tee which is located at the top of the column. The temperature of the HCl mist is 18°C. and it is kept essentially constant at this temperature while the gas is contacted with it. Vapor pressure of the HCl solution is 5.0 mm Hg and the ratio of the surface area of the HCl mist to the weight of $TiCl_4$ is about 2.6 m^2 surface area per gram. HCl and gas are circulated cocurrently through the column at rates of 108 gallons per hour and 32 standard cubic feet per hour, respectively. After the gas is discharged from the bottom of the column, it is scrubbed with water to remove any HCl present. Then, the gas is vented to the atmosphere.

As the gas is vented to the atmosphere, essentially no fumes are visible. Analysis of the acid shows that the soluble titanium content has increased to 2.2 weight percent which means that the HCl absorbed $TiCl_4$ from the gas containing $TiCl_4$. Essentially all of the $TiCl_4$ is absorbed since the gas vented to the atmosphere does not appear as a white cloud.

EXAMPLES 2—11.

Example 1 is repeated under the conditions listed in Table 1. HCl mist was used in all cases.

TABLE 1

Example	HCl Conditions			Wt. % Soluble Ti Initially in the HCl	Wt. % Soluble Ti in HCl after contact with the Gas	Did the gas fume when vented to the atmosphere after contact with HCl?
	Wt. % HCl	Temp.	Vapor Pressure (mm Hg)			
2	24	–3°C.	1.6	0.20	0.25	No
3	29	9°C.	2.7	2.0	2.2	No
4	24	3°C.	2.8	0.08	0.19	No
5	30	12°C.	3.0	0	0.02	No
6	27	9°C.	3.2	2.01	2.18	No
7	34	18°C.	3.2	1.93	2.18	No
8	25	8°C.	3.4	0.08	0.20	No
9	27	11°C.	3.6	0.02	0.08	No
10 (comparison)	29	25°C.	7.6	2.18	2.20	Yes
11 (comparison)	24	25°C.	11	2.18	2.20	Yes

In Examples 10 and 11, the gas fumed when vented to the atmosphere, which shows that $TiCl_4$ is not effectively removed from the gas when the vapor pressure of the acid is too high.

EXAMPLES 12—16.

If the procedure of Example I is repeated using the mists and conditions listed in Table 2, the indicated results would be obtained.

TABLE 2

	Mist Conditions						
Example	Mist	Wt. %	Temp.	Vapor Pressure (mm Hg)	Projected Wt. % Ti Initially in the Mist	Projected Wt. % Ti in the Mist after Contact with Gas	Would the gas fume when vented to the atmosphere after contact with the Mist?
12	HNO_3	70	23°C.	4.94	0	0.11	No
13	$FeCl_3$	30	0°C.	4.1	0	0.12	No
14 (comparison)	$FeCl_3$	30	23°C.	19.2	0	0.06	Yes
15	NaCl	30	0°C.	4.1	0	0.12	No
16 (comparison)	NaCl	30	23°C.	19.4	0	0.06	Yes

In Examples 14 and 16, the gas would fume when vented to the atmosphere because the $TiCl_4$ would not be effectively removed from the gas when the vapor pressure of the mist is above the limits set out for this invention.

WHAT WE CLAIM IS:—

1. A process for removing halide vapour from a waste gas which process comprises (A) generating an absorptive aqueous mist containing water in which is dissolved one or more of HCl, HNO_3, HBr, HF and HI and/or one or more halide salts of the following cations, namely calcium, sodium, ammonium, lithium, barium and iron; (B) bringing the waste gas into contact with the absorptive aqueous mist, the

temperature of the combined waste gas stream and absorptive aqueous mist being maintained from $-5°C.$ to $70°C.$, the water vapour pressure of the absorptive aqueous mist being maintained at from 0.05—5 mm Hg prior to and during the contact and the particle size of the aqueous absorptive mist being such that the ratio of the surface area of the absorptive aqueous mist to the weight of the halide to be removed is at least two square meters surface area of the absorptive aqueous mist per gram of halide; and (C) effecting additional processing to remove mist from the gas/mist mixture and to remove halide acid from the gas.

2. A process according to Claim 1 wherein the halide vapour is vapour of one or more of the following halides, namely the halides of titanium, aluminium, vanadium, silicon, tin, magnesium, zinc, antimony, sulfur, phosphorous and ammonia.

3. A process according to Claim 1 or Claim 2 wherein the ratio between the surface area of the aqueous mist to the weight of waste halide is 12 to 16.

4. A process according to Claim 2 wherein the halide is titanium tetrachloride.

5. A process according to Claim 2 wherein the halide is silicon tetrachloride.

6. A process according to any one of the preceding claims wherein HCl is dissolved in the aqueous mist.

7. A process according to any one of the preceding claims wherein sodium chloride is dissolved in the aqueous mist.

8. A process for removing halide vapour from a waste gas containing one or more of the following halides in vapour form, namely, the halides of titanium, aluminium, vanadium, silicon, tin, magnesium, zinc, sulfur, antimony, phosphorous and ammonia which process comprises forming an absorptive aqueous mist comprising mist particles comprised of water in which is dissolved one or more of HCl, HNO_3, HBr, HF and a salt of formula MX in which M is an equivalent of one of the following cations, namely calcium, sodium, ammonium, lithium, barium and iron and X is an equivalent of a halide anion; delivering the preferred absorptive aqueous mist and said waste gas to a contact zone and effecting contact therein of one with the other to cause absorption of halide vapour into said mist, the temperature of the combined waste gas stream and absorptive aqueous mist being maintained at from $-5°C.$ to $70°C.$, the water vapour pressure of the absorptive aqueous mist being maintained at from 0.05—5mm Hg prior to and during the contact so that the halide vapour is absorbed by the mist without reaction of halide and mist to form particles of reaction product, and the particle size of the aqueous absorptive mist being such that the ratio of the surface area of the absorptive aqueous mist to the weight of the halide to be removed is at least two square meters surface area of the absorptive aqueous mist per gram of halide; and effecting additional processing to remove mist from the gas/mist mixture and to remove halide acid from the gas.

9. A process for removing waste halide vapour from a waste gas stream, substantially as described in any one of Examples 1 to 9, 12, 13 and 15.

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