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(54) **Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products.**

(57) The process for treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum-products is based on the synergical use of ozone and calcium hypochlorite. More specifically, the process according to the present invention consists essentially in subjecting the spent aqueous solutions of caustic soda to the following operations :

— a first oxidization using 0,5-3,5 Kg of O_3/Kg of total phenols, at a temperature of between 38 and 42°C ;

— a second oxidation with 5-10% by weight of calcium hypochlorite, referred to the previously ozonized spent caustic soda, at a temperature selected from the range of between 25 and 35°C, with the formation of a pulp with a flaky suspension ; and

— separation of the pulp formed into a liquid phase and a solid phase, each of which can be eliminated in a much easier and safer way, from an ecological point of view, than the initial spent solution of caustic soda.

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The present invention relates to a process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products ("spent caustics"), based on the synergical use of ozone and calcium hypochlorite. The treatment according to the invention allows reduction of the pollution load of the spent solutions of caustic soda, obtaining two final streams which, as they are or after further routine treatment, are compatible with the ecological specifications of national and international laws regarding emission of substances into the atmosphere, water discharge and final solid waste destined for disposal in authorized waste disposal centers.

As is known, many intermediate and final streams from plants for the processing of petroleum products contain a variety of acid compounds such as hydrogen sulphide (sulphydric acid), mercaptans, phenols, thiophenols and naphthenic acids. These substances must be removed or brought down to specific concentrations. The compounds containing sulphur must be reduced to low concentrations in order to satisfy customs and merchant specifications, or to improve the "octane number" of the petrol. Sulphydric acid and phenols must be removed to prevent them from interfering with successive processes for reduction of mercaptans. Naphthenic acids must be removed to obtain the clearly defined specifications regarding acidity of certain fuel products.

For the removal of the above undesired compounds, aqueous solutions of NaOH are usually used, in concentrations of between 5 and 15% by weight (fresh caustic).

The spent caustic soda solution obtained has a different composition dependent on whether it has been used for purification of LPG (propane and butane), of petrols obtained from thermal and/or catalytic "cracking", or of "straight-run" petrols (obtained from distillation of crude oil at atmospheric pressure), bearing in mind the conventional treatments which these products undergo.

In general the spent caustic soda solutions have pH values ranging from 12,5 to 13,5 and the following composition expressed in percentage by weight:

free caustic soda	5,0-7,5
total oils	0,5-2,0
total sulphides	0,1-3,0
cyanides	0,05-0,3
ammonia	0,05-0,4
phenols	0,2-10
lead	2.10^{-4}-10.10^{-4}
arsenic	1.10^{-4}-5.10^{-4}
copper	5.10^{-4}-50.10^{-4}
cadmium	1.10^{-4}-5.10^{-4}

the balance being water.

From the state of the art of this specific field it is known that the conventional technology relating to treatment of "spent caustics" from the petroleum and petrol-chemical industry is based on their neutralization using mineral acids (for example sulphuric acid and hydrochloric acid) or using gases containing carbon dioxide and sulphur dioxide.

According to this technology, when the solution of spent caustic soda is neutralized (or "sprung", as this operation is commonly known), two distinct layers are formed: a lower aqueous layer containing the sodium salts of the neutralizing acid, called "sprung-water", and an upper oily layer containing phenolic compounds which are given various names in this sector, the commonest of which is "sprung-acid".

This technology, although amply consolidated, is not entirely satisfactory from an environmental point of view. In fact, it involves highly exothermic reactions, accompanied by a notable pH jump (from pH 12-13 to pH 4-5) and the production of gaseous effluents which require the use of successive thermo-destructive processes. Furthermore, this is an extremely costly technique due to the special nature of the metallic materials to be employed in the processing plants and due to the need for final sour-water stripping interventions and consequent final thermodistruction of the stripping residue.

Given the above, there is in this field a need for a process which makes it possible to overcome the above mentioned drawbacks.

The process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products according to the present invention makes it possible to avoid all the disadvantages found in the state of the art, furthermore offering other advantages which will be made clear in the following.

The process according to the invention is based, generally speaking, on the synergical action of ozone and calcium hypochlorite on the undesired products found in spent caustics.

More specifically, the process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products, is characterized in that the spent solutions of caustic soda are subjected essentially to the following operations:

- a first oxidization with 0,5-3,5 Kg of O_3/Kg of total phenols, at a temperature in the range of 38-42°C;

- a second oxidization with 5-10% by weight of calcium hypochlorite, with reference to the previously ozonized spent aqueous solution of caustic soda, at a temperature selected from the range of 25-35°C, with the formation of a pulp with a flaky suspension; and
- separation of the pulp into two phases, a liquid phase and a solid phase, each of which can be eliminated in a much easier and safer way, from an ecological point of view, than the initial solution of spent caustic soda.

It has been seen that the first oxidization is accompanied by a strong oxidating demolition of the phenolic ring and by a partial oxidation of the compounds containing sulphur, until obtaining much less toxic molecules (for example oxalic acid, carbon dioxide, oxygen, water and sulphur). The second oxidation stage promotes the breakage of the R-SH bond and the formation of sulphur molecules in the form of a flaky aggregate which is subject to sedimentation. The liquid phase produced by this separation is of a reddish colour and has a slight smell of phenols; it is suitable for routine treatments. The solid phase obtained after separation of the pulp is dark yellow in colour, flaky in aspect, and a slight smell of compounds containing sulphur; it is suitable for final disposal in waste disposal dumps and/or for controlled recovery as inert re-cycled material.

In the process according to the present invention, the calcium hypochlorite can be added as it is or formed on site, for example by means of a reaction between sodium hypochlorite and lime.

Phase separation, in the process according to the present invention, can be obtained using an operation chosen from the group comprising: centrifugation, optionally under vacuum; filtering, optionally under vacuum; filter pressing; and band-pressing.

In the above, a description of a general nature has been given of the process object of the present invention. There will now be given, with the aid of an example, a more detailed description of a preferred form of realization, with the aim of rendering objectives, characteristics, advantages and function more clear.

EXAMPLE

The spent aqueous solution of caustic soda which is to undergo treatment according to the present invention was obtained from the washing of " straight-run" refinery petrol. This solution cannot be disposed of as it is, because its pH value is 13 and it contains a high pollution load. In particular, it contains the following:

total phenols	20.000 ppm
total compounds containing sulphur (sulphides and mercaptans)	30.000 ppm
total cyanides	1.000 ppm
total nitrogen	500 ppm
chlorides	20.000 ppm
other chemical compounds	25 ppm

(by "other chemical compounds" are intended carbonates, sulphites, sulphates and heavy metals such as lead, arsenic, copper and cadmium).

After homogenization in a suitable homogenizing container, this solution is subjected to a first oxidization step with 2 kg of O_3/kg of total phenols. A progressive change in colour of the solution can be seen, turning from dark brown to a lighter shade of brown; at the same time the intense and pungent smell of phenol and organic substance tends to grow less. The pH value goes down from 13 to approximately 10. The process is accompanied by an increase in temperature up to 38-40°C and by an intense physiological foaming, which grows noticeably less on the controlled addition of an antifoaming agent. The second oxidization step is then performed, adding 6% by weight of calcium hypochlorite, with reference to the ozonized spent aqueous solution of caustic soda. The formation of dark yellow flakes can be noted, and these tend to sediment, generating a pulp of a colour tending towards dark yellow. There is no emanation of particular smells. The flakes are characterized by a high level of sedimentation.

The pulp is made to undergo centrifugal separation by means of an horizontal mechanical two-way decanter. A liquid phase and a solid phase are obtained. In the liquid phase, red in colour, with a not particularly intense

smell of phenol, a reduction of the content in phenols, sulphides and mercaptans is registered of about 90% with respect to the starting values. This stream, as it is or after further treatment, is suitable for disposal using current refinery and petrol-chemical waste disposal technology.

The centrifuged solid phase, with a dryness of 35% by weight, results easy to shovel and is compatible with the other factory waste, as it can be integrated in the pre-treatment system to be adopted for said waste, before final disposal. In particular this residual solid stream can be classified, e.g. according to the Italian Law (DPR 915/82 and the deliberation by the C.I. dated 27/7/84), as special waste. It can therefore be disposed of, after solidification/stabilization by the addition of lime and silicates, as such or together with the pool of special refinery waste, deriving from purification sludge of a chemical-physical and biological nature.

Claims

1. Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products, characterized in that the spent solutions of caustic soda are subjected essentially to the following operations:
   - a first oxidization with 0,5-3,5 Kg of O_3/Kg of total phenols, at a temperature in the range of 38-42°C;
   - a second oxidization with 5-10% by weight of calcium hypochlorite, with reference to the previously ozonized spent aqueous solution of caustic soda, at a temperature selected from the range of 25-35°C, with the formation of a pulp with a flaky suspension; and
   - separation of the pulp into two phases, a liquid phase and a solid phase, each of which can be eliminated in a much easier and safer way, from an ecological point of view, than the initial solution of spent caustic soda.

2. Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products according to the previous claim, in which the calcium hypochlorite is added as it is to the spent aqueous solution of caustic soda.

3. Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products according to claim 1, in which the calcium hypochlorite is formed on site.

4. Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products according to claim 3, in which the calcium hypochlorite is formed on site by means of reaction between sodium hypochlorite and lime.

5. Process for the treatment of spent aqueous solutions of caustic soda used for purification and washing of petroleum products according to any one of the preceding claims, in which separation of the pulp into two phases, a liquid phase and a solid phase, is obtained by means of an operation selected from the group comprising: centrifugation, optionally under vacuum; filtering, optionally under vacuum; filter-pressing; and band-pressing.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 83 0030

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-859 286 (U.O.P.)	1	C10G19/08
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 JUNE 1992	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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