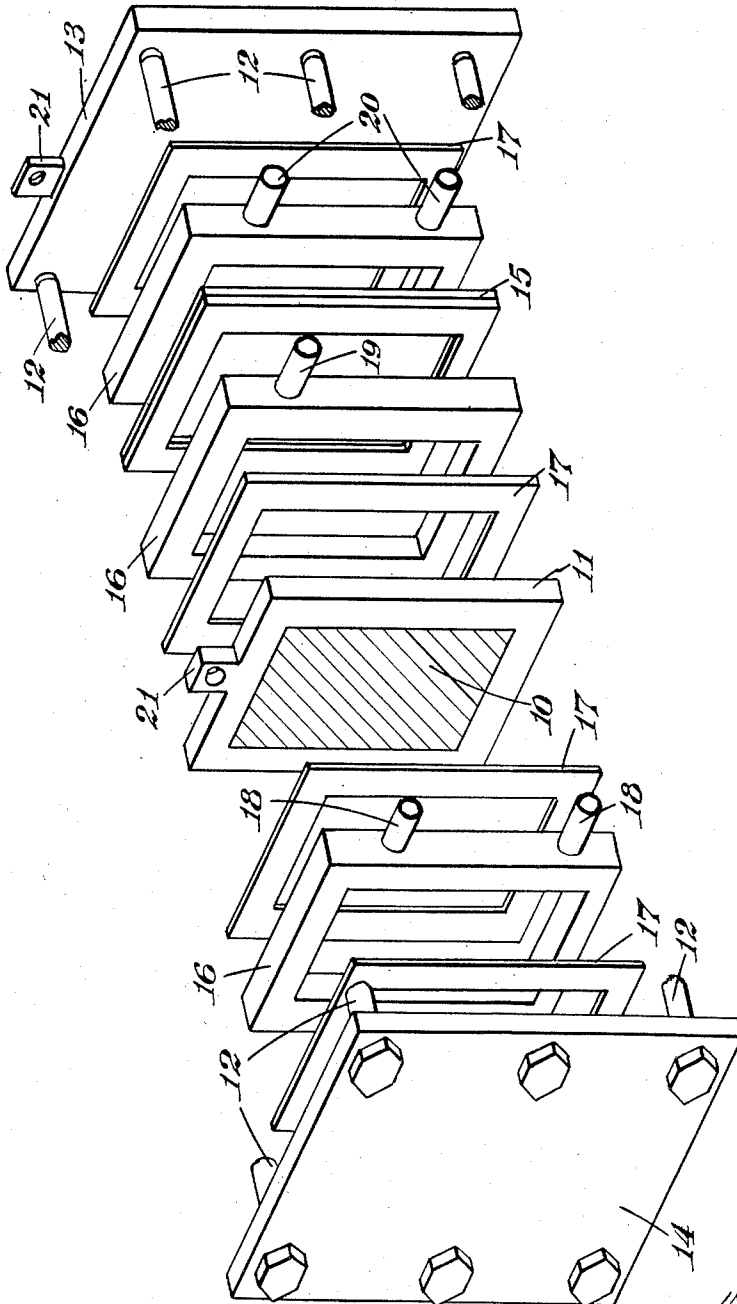


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ELECTROLYTIC REGENERATION OF AQUEOUS
SOLUTIONS CONTAINING MERCAPTIDES
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ELECTROLYTIC REGENERATION OF AQUEOUS SOLUTIONS CONTAINING MERCAPTIDES

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1 Claim. (Cl. 204—153)

This invention relates to the electrolytic regeneration of aqueous alkaline solutions containing mercaptans dissolved as mercaptides.

The lighter fractions obtained on distilling crude petroleum oil are often washed with caustic soda solutions or other alkaline reagents with the object of removing mercaptans. These solutions are preferably regenerated and re-used to avoid difficult disposal problems and wastage of chemicals. One known method of regeneration is to pass an electric current through the solution so that the mercaptide ions are oxidised at the anode. It is desirable that the mercaptans shall be oxidised to disulphides as these are insoluble in the treating solution and can be separated by suitable means. Unless the oxidation is carefully controlled the products do not consist entirely of disulphides but comprise more highly oxygenated compounds such as sulfoxides and sulphonates and in addition free oxygen may be evolved. These are all undesirable because they waste the electric current; in addition, the more highly oxygenated compounds are water soluble and result in a deterioration of the alkaline extraction solution.

We have found that the current efficiency increases with decreasing current density, and that electrode metal such as platinum with a high oxygen over-voltage is much less satisfactory than a metal such as nickel with a low oxygen over-voltage. These experimental facts can be explained by assuming that the discharge of mercaptide ions constitutes the mechanism of the reaction (i. e. not the intermediate formation of peroxide) and that the discharge voltage of the mercaptide ions is lower than that of hydroxyl ions. Use of voltages much higher than that required to discharge the mercaptide ions will result in excessive oxidation and also formation of gaseous oxygen. Such unnecessarily high voltages may result from too high a current density or from using an unsuitable electrode with a high oxygen over-voltage. The use of the lowest possible voltage is also a desirable end in itself as it reduces the power requirements.

While the provision of a suitable anode material with a low oxygen over-voltage is not difficult, it is less easy to provide a sufficiently large anode area in conventional cells. A filter press type of cell is commonly used for electrolytic oxidations and reductions and when a large surface area is required, the electrodes are corrugated and may have attached to them metal gauze screens or similar material in attempts to increase the effective surface area. It is also known to insert, in conductive contact with each side of the anode plate, a foraminous body, such as a stack of fine mesh wire sheets, compressed knitted metal, or loosely compressed metal fibres or powder. Such artifices can only be completely successful when the electrolyte is dispersed evenly over the total available surface area so that all parts of it are equally effective.

We have found that by passing the electrolyte through an anode made of sintered metal, the necessary even dis-

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tribution of electrolyte over a relatively large surface area is secured.

The invention therefore consists in using a sintered metal anode in the electrolytic regeneration of aqueous alkaline solutions containing mercaptides.

Advantageously a sintered nickel anode is used.

If the same current is applied to a cell of the type hitherto used and also to a cell with a sintered anode of the same outside dimensions, the increased surface area and hence lower current density is reflected in much greater current efficiency and lower voltage drop.

The solution to be regenerated is advantageously made to pass through the sintered metal anode.

The invention will now be described by way of example with reference to the accompanying drawing which is an exploded view of an electrolytic cell with a sintered anode.

The sintered metal anode 10 is supported in a rectangular iron frame 11 which is clamped by means of 6 tie rods 12 between end plates 13 and 14. End plates 13 acts as the cathode. A diaphragm 15 is provided between the anode and cathode. The diaphragm is almost impermeable to gas under the experimental conditions and it also effectively limits liquid circulation between anode and cathode compartments on either side of it. The various parts of the cell are separated by spacing members 16 consisting of rectangular metal frames. The cell is made leak-proof by the provision of sealing gaskets 17 between the metal surfaces, the gaskets also serving to insulate the anode from the cathode. The anolyte is supplied to the cell through pipes 18, i. e. on the side of the anode remote from the cathode, and is withdrawn by pipe 19 from the space between the anode and diaphragm. The liquid in the cathode compartment is circulated by means of pipes 20 to a hydrogen separator. The anode and cathode are provided with lugs 21 for making the electrical connections.

The invention is illustrated by the following experiments:

EXPERIMENT 1

A solution containing isopropyl mercaptan in 10 percent w./v. caustic soda was used in each case. In the first experiment the solution was passed at the rate of about 4 litres/hour through a single unit filter press type electrolytic cell with an impressed current of 5 amperes and a current density of 48 amps./sq. ft. The inlet and outlet mercaptan sulphur contents were 0.233 percent w./v. and 0.207 percent w./v. respectively and the current efficiency was 19 percent. In the second experiment a sintered nickel anode was inserted in the cell and the solution was pumped through at a rate of about 1 litre/hour, the current being 2 amperes. The inlet and outlet mercaptan sulphur contents were 0.214 percent w./v. and 0.037 percent w./v., the current efficiency being 76 percent. Thus the sintered anode was four times as efficiency as a plain anode when working under less favourable conditions, i. e. a lower mercaptan content product.

EXPERIMENT 2

Caustic extraction of a Middle Eastern straight-run gasoline feedstock was carried out in a glass three-stage washery. Two runs were carried out. In each case a 25% vol. caustic treatment was given and in each case the mercaptan sulphur content of the feedstock was 0.04% wt. and of the treated oil 0.01% wt. approximately when the unit reached equilibrium.

In the first run, the mercaptan-rich caustic was pumped to an electrolytic cell having a smooth nickel anode. In the second run, it was pumped to the above-described and illustrated cell with a sintered anode. The cell with the

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smooth nickel anode was of the same size and construction as the cell with the sintered anode except that there was no compartment on the side of the anode remote from the cathode and the anolyte was pumped to and removed from the space between the smooth anode and the diaphragm.

The following table illustrates the superiority of the sintered anode.

Table

	Run 1	Run 2
Type of anode.....	Smooth Nickel	Sintered Nickel
Average mercaptan sulphur content of caustic feed to cell, percent wt.....	0.14	0.15
Average mercaptan sulphur content of regenerated caustic, percent wt.....	0.06	0.08
Feed rate, litres/hour.....	1	1
Impressed current, amps.....	5	1
Current density, amps./ft. ²	48	19.3
Current efficiency, percent.....	10	60
Ampere hours per lb. sulphur converted.....	3,790	632
Voltage drop, volts.....	3.6	2.3
Kwh./lb. sulphur converted.....	13.6	1.43
Caustic soda consumed, lb./1,000 galls. oil.....	2.0	0.18
Kwh./1,000 galls. oil.....	27.5	3.10

¹ Arbitrary figure based on an anode of 3" x 5". When using the sinter the true area is very much greater than 15 sq. in. but is unknown.

When using the cell with the sintered anode it was necessary to use a higher impressed current than with the

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cell having a plain anode in order to keep the mercaptan contents of the caustic comparable in the two cases. The superiority of the sintered anode is clearly shown particularly by the figures for power consumption and caustic soda consumed.

We claim:

A process for the electrolytic regeneration of aqueous alkaline solutions containing mercaptans comprising passing the solution to be regenerated through an anode in substantially solid form, and made of sintered nickel whereby an even distribution of the solution to be regenerated over a relatively large surface area is obtained, with a corresponding reduction in power consumption and caustic soda consumption resulting.

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