

## PATENT SPECIFICATION

NO DRAWINGS

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1.115.608

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## COMPLETE SPECIFICATION

## Process for the Separation of a Wax-containing Mixture

We SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organized under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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:—

10 The invention relates to a process for the separation of a wax-containing mixture by cooling the mixture in the presence of a diluent comprising at least one ketone, separating wax crystallized by such cooling, 15 recovering diluent from said wax and/or from the non-crystallized portion of the mixture, and recycling recovered diluent to the cooling step.

20 Process of this kind, employing the diluents in question, are widely on a commercial scale, since they have been found to be very suitable for the preparation of e.g. starting materials for the manufacture of lubricating oil or wax in an economical manner. It has 25 been found, however, that they possess a serious drawback in that the diluent employed becomes very corrosive in use, leading to severe attack upon the materials of construction employed in building the separation 30 equipment.

35 It would, of course, be possible to renew the diluent inventory as soon as it has become unacceptably corrosive, or to withdraw a slip stream of the corrosive diluent and replace it with fresh; however, since corrosivity has been found in the diluent to a very large extent already after a short period of use, diluent renewal would have to be repeated often, or alternatively, the slip stream 40 withdrawn would have to comprise a large part of the total quantity of diluent present,

so that such measures would seriously affect the economics of the process. The use of corrosion inhibiting or removing agents in the diluent or on the equipment, on the other hand, if at all effective, may well lead to an unacceptable level of impurities in the products obtained, and can therefore often not be tolerated either.

45 It has now been found that there is a simple, effective, and economical way of dealing with this corrosivity problem; for it has turned out that the corrosive compounds present in the diluent can be removed from it in a very simple manner.

50 Hence, the invention relates to a process for the separation of a wax-containing mixture in the presence of a diluent comprising at least one ketone, separating wax crystallized by such cooling, recovering 55 diluent from said wax and/or from the non-crystallized portion of the mixture, and recycling recovered diluent to the cooling step, in which at least part of said recovered diluent is contacted with an absorbent before 60 being recycled to the cooling step.

65 This adsorptive treatment is much more effective than the removal of corrosive compounds, e.g. by distillation, which on the one hand can only remove those compounds boiling in a different range than the diluent itself, and on the other hand always leads to losses of diluent, which is removed together with the corrosive compounds; 70 furthermore, the disposal of the very corrosive streams so obtained is beset with difficulties.

75 It has furthermore been ascertained that those substances which show some preference for adsorbing polar compounds are especially suitable for removing corrosivity from circulating diluent; this is rather surprising, for 80

offhand one would expect that such contact materials would adsorb the diluent itself, since this is at least in part polar. This would, of course, lead to diluent losses, and also to a substantial loss in adsorbent capacity for the corrosive compounds to be removed; however, contrary to all expectation, substantially no adsorption of the diluent material itself has been found to occur in practice. Among the suitable adsorbents there may be cited several types of clay, fuller's earth, silica gel, silica-alumina and molecular sieves. Alumina, especially in its activated form, is most preferably employed, since it has been found to be very efficient.

In principle, the adsorbent may be used in any desired size and shape, usually dependent on the manner in which contacting with the diluent is effected. This can e.g. be done by stirring the adsorbent with the diluent to be cleaned, followed by separation of adsorbent and diluent, in which case the adsorbent is suitably in powder form. It is preferred, however, to employ a bed of adsorbent (which can e.g. be a moving bed, but is preferably a fixed bed), since this allows for continuous operation; in this case, the adsorbent is suitably in the form of granules, such as extrudates or pellets. A preferred size for such a granular adsorbent is about 0.5—1 mm, although different, e.g. coarser particles can also be used.

The contacting temperature of adsorbent and diluent can be chosen at will; it has been found that an efficient removal of corrosive compounds can be obtained at ambient temperature, which is therefore preferred, as being the most economical.

It has further been ascertained that residence times (calculated as the volume of adsorbent employed, divided by the volume of diluent passed in contact with this adsorbent per minute) of 15 minutes or less are generally sufficient for effecting substantially complete removal of corrosive compounds; in many cases, residence times of e.g. up to 7.5 minutes may already suffice.

Although it is possible to contact all the diluent recovered with the adsorbent, it has been found possible to remove corrosivity to a sufficient extent by subjecting only a minor part of this diluent to the adsorbing treatment; generally, only 8—12% of the recovered diluent need be so contacted, the remainder being recycled directly to the cooling step of the separation.

After some time, depending inter alia on the nature of the adsorbent employed and on the content of corrosive compounds in the diluent being treated, the adsorbent's capacity for further removal of corrosive compounds diminishes, as can be easily determined by subjecting the diluent issuing from the contacting step to any of the known corrosivity measuring methods. It is, of course, possible

to replace adsorbent which is spent to an intolerable extent by fresh adsorbent, which however, is not a very economical procedure. It has been found that such spent adsorbent can easily be regenerated, e.g. by steaming out, if desired with superheated steam, leading to a substantial restoration of its corrosivity removing capacity, so that it can be re-used in the process. On the other hand, the used steam, and especially the water obtained by its condensation, have been found to have become very corrosive themselves, leading to difficulties in their disposal. Therefore, a different method of regeneration is preferred, viz. the regeneration of adsorbent which is spent to an undesirable degree by contacting it with an alkaline liquid, preferably at ambient temperature as well. Such liquids have been found not to become corrosive after use. It has been found that after this type of regeneration, the capacity of the adsorbent may be even better than that when fresh; suitably, therefore, fresh adsorbent to be employed for the first time is pretreated with an alkaline liquid already before use, preferably with the same type that is later to be used for regeneration, and suitably also at ambient temperature.

For regeneration, as well as for pretreatment (if effected), relatively small quantities of alkaline liquid may suffice; for instance, in many cases it is sufficient to employ 0.5—3 volumes of this liquid per volume of adsorbent. It is often possible to use the alkaline liquid repeatedly; also, such a liquid which has already been applied once or several times can subsequently be used for some other purpose, e.g. for contacting a material requiring an alkaline treatment (e.g. hydrogen and/or hydrocarbon gases containing acid impurities, and normally liquid hydrocarbon materials, such as gasolines, kerosines, lubricating oils or crude oils).

Very suitable alkaline liquids, to be used as regenerating and/or pretreating liquid, are those comprising alkaline earth metal hydroxides especially milk of lime, and/or alkali metal carbonates, such as aqueous sodium carbonate solutions, e.g. having a 1.5—2.5%wt carbonate content, and/or alkali metal hydroxide solutions, such as 1%wt aqueous sodium hydroxide.

The pretreated or regenerated adsorbent which has been contacted with alkaline liquid may subsequently be dried, suitably by means of a substantially dry gas (e.g. air, nitrogen) at elevated temperature; the adsorbent may, if desired, be steamed out before drying.

Preferred diluents employed in the present process are those comprising methyl ethyl ketone, suitably in admixture with at least one aromatic compound, e.g. toluene. Another very suitable ketone is methyl isobutyl ketone.

The starting mixtures to be treated according to the invention may be e.g. those con-

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taining wax and oil which are to be separated from each other, such as oily waxes and waxy oils; they may also be mixtures of waxes which must be separated. With all these mixtures, applying the process of the invention is of great advantage.

The invention will be further elucidated by means of the following Examples.

#### EXAMPLE I

A sample comprising methyl ethyl ketone and toluene, obtained from the diluent stream being recycled to the cooling step of a dewaxing operation, was found to be extremely corrosive, as indicative by a weight loss of 85 mg per square decimetre per day in a mild steel test piece in contact with the sample, the latter being kept in air at 100°C. When a slip stream of the same diluent was passed through a bed of granulated clay at ambient temperature, corrosivity was found to be fully removed. After 3—4 volumes of diluent per volume of clay had been treated, the corrosivity removing capacity of the clay was exhausted, the corrosivity of a sample of the bed effluent being substantially the same as that of the untreated stream; the bed was then regenerated by steam, which caused some damage to the clay granules, resulting in the bed becoming clogged by fines; this adsorbent, although quite effective when being contacted batchwise with corrosive diluent, was therefore considered less suitable for continuous use in a bed.

Similar results were obtained with activated fuller's earth and silica gel.

#### EXAMPLE II

A slip stream of the same circulating diluent of Example I was passed downwardly through a vertically disposed bed of activated alumina at ambient temperature and at a residence time of 6 minutes. The corrosivity of the bed effluent was reduced by a factor of 100, as compared to that of the untreated diluent. The corrosion removing capacity of the adsorbent was exhausted only after 23 parts by weight of diluent per part by weight of alumina had been treated. In order to regenerate the adsorbent, the bed was heated to 150°C, steam being passed through, and subsequently condensed, until the condensate was no longer corrosive; the bed was then dried by means of nitrogen heated to 100°C. The corrosivity removing capacity of the bed was restored to substantially the same value as before regeneration; the bed could be re-used and regenerated at will, without any decrease in efficiency and without any damage to the adsorbent particles.

In another experiment, regeneration was not carried out by steaming, but by treatment at ambient temperature with an alkaline liquid. Only 1—2 volumes per volume of adsorbent of a 2%wt sodium carbonate solution, and

subsequent drying with air at 150°C, effected regeneration to a degree even exceeding the corrosivity removing capacity of the adsorbent when fresh; for upon regeneration, this capacity was exhausted only after as much as 50 parts by weight of diluent per part by weight of alumina had been treated. Substantially the same result was obtained after repeated regenerations, no damage to the adsorbent particles being observed.

In yet another experiment, regeneration was carried out by treating the adsorbent with milk of lime (in this case containing 0.5%wt of calcium hydroxide). After this type of regeneration, the corrosivity removing capacity of the adsorbent was exhausted only after 69 parts by weight of diluent per part by weight of adsorbent had passed through. In this case also re-use and regeneration could be repeated at will, with similar results being obtained and no damage being observed.

#### EXAMPLE III

Some experiments were carried out with a slip stream of the same circulating diluent of the previous Examples, passed at ambient temperature through a bed of fresh activated alumina which had been pretreated by 1—2 bed volumes of 2%wt aqueous sodium carbonate, at various residence times. The capacity of the adsorbent for removing corrosive compounds was measured as parts by weight of diluent passed through per part of adsorbent before the latter became spent. The capacity results are shown in the following Table:

| Residence time, min. | Capacity, pbw of diluent/pbw of alumina |
|----------------------|-----------------------------------------|
| 2                    | 3                                       |
| 6                    | 42                                      |
| 7½                   | 56                                      |

#### EXAMPLE IV

Some experiments were carried out with a slip stream of the same circulating diluent and the same pretreated adsorbent as in Example III, at a residence time of 11 minutes and at various particle sizes of the adsorbent.

When employing 8 mm pellets, after 7½ parts by volume per part by volume of adsorbent had been treated the adsorbent was already exhausted to such an extent that the bed effluent was about 40% as corrosive as the untreated diluent; when granules of 2—3½ mm were employed, a similar degree of exhaustion was reached only after 34 parts by volume of diluent per part by volume of adsorbent had been treated. When applying 0.5—1 mm granules, on the other hand, after treating the same quantity of 34 parts by volume of diluent per part by volume of adsorbent, the bed effluent was still wholly devoid of corrosivity.



## WHAT WE CLAIM IS:—

1. Process for the separation of a wax-containing mixture by cooling the mixture in the presence of a diluent comprising at least one ketone, separating wax crystallized by such cooling, recovering diluent from said wax and/or from the non-crystallized portion of the mixture, and recycling recovered diluent to the cooling step, characterized in that at least part of said recovered diluent is contacted with an adsorbent before being recycled to the cooling step.
2. Process according to claim 1, characterized in that an adsorbent is employed of a type which preferentially adsorbs polar compounds.
3. Process according to claim 2, characterized in that alumina is employed as adsorbent.
4. Process according to claim 1, 2 or 3, characterized in that said adsorbent is employed in the form of granules having a size of 0.5—1 mm.
5. Process according to any one of claims 1—4, characterized in that said contact is carried out at ambient temperature.
6. Process according to any one of claims 1—5, characterized in that said diluent is contacted with the adsorbent at a residence time of at most 15 minutes.
7. Process according to any one of claims 1—6, characterized in that 8—12% of said recovered diluent is contacted with adsorbent, the remainder being directly recycled to the cooling step.
8. Process according to any one of claims 1—7, characterized in that said adsorbent is regenerated by being contacted with an alkaline liquid.
9. Process according to any one of claims 1—8, characterized in that said adsorbent, when fresh, is pretreated by being contacted with an alkaline liquid.
10. Process according to claim 8 or 9, characterized in that said alkaline liquid comprises an alkali earth metal hydroxide.
11. Process according to claim 10, characterized in that said alkaline liquid is milk of lime.
12. Process according to claim 8 or 9, characterized in that said alkaline liquid comprises an alkali metal carbonate.
13. Process according to claim 12, characterized in that said alkaline liquid is a 1.5—2.5%w aqueous sodium carbonate solution.
14. Process according to any one of claims 8—13, characterized in that 0.5—3 volumes of alkaline liquid are employed per volume of adsorbent.
15. Process according to any one of claims 8—14, characterized in that said contact with an alkaline liquid is carried out at ambient temperature.
16. Process according to any one of claims 8—15, characterized in that the regenerated adsorbent is subsequently treated with a substantially dry gas at elevated temperature.
17. Process according to any one of claims 1—16, characterized in that said diluent comprises methyl ethyl ketone.
18. Process according to any one of claims 1—17, characterized in that said diluent further comprises at least one aromatic compound.
19. Process according to any one of claims 1—18, characterized in that said wax-containing mixture is a waxy oil.
20. Process according to any one of claims 1—18, characterized in that said wax-containing mixture is an oily wax.
21. Process according to any one of claims 1—18, characterized in that said wax-containing mixture is a mixture of waxes.
22. Process for the separation of a wax-containing mixture, substantially as hereinbefore described, with special reference to the Examples.
23. Waxes, oils, and mixtures comprising them, whenever obtained by means of the process according to any one of claims 1—22.

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## ERRATA

## SPECIFICATION No. 1,115,608

- Page 1, line 19, for "Process" read "Processes"  
Page 1, line 20, after "widely" insert "used"  
Page 1, line 58, after "mixture" insert "by cooling the mixture"  
Page 1, line 65, for "absorbent" read "adsorbent"  
Page 2, line 121, for "substantially" read "substantially"  
Page 3, line 39, Example II, for "vertically" read "vertically"

THE PATENT OFFICE  
5th July 1968

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