Patented May 9, 1939 2,157,294

UNITED STATES PATENT OFFICE

2,157,294

MERCERIZING LYES AND A PROCESS FOR THEIR MANUFACTURE

Heinrich Lier, Basel, Switzerland, assignor to the firm of Chemical Works Formerly Sandoz, Basel, Switzerland

No Drawing. Application January 7, 1937, Serial No. 119,528. In Switzerland January 9, 1936

8 Claims. (Cl. 8—127)

The present invention relates to a process for improving the wetting-out properties of alkaline lyes of at least 18° Bé. and to such improved lyes and is based on the use of naphthenic acids as such or in combination with emulsifying agents of non-phenolic character or with amino- or ether alcohols.

Until now it has only been known that naphthenic acids which are a by-product in the manufacture of petrol can be used in dilute alkaline solutions the specific gravity of which is not higher than 1° Bé. It has always been thought that these acids cannot be used in concentrated lyes because of their poor solubility.

The present invention resides on the observation that naphthenic acids can very well be used alone as wetting agents in concentrated alkaline lyes say from 18° Bé. upwards, if their molecular weight or their acid number is adapted to the concentration of the lye.

According to the present invention concentrated alkaline lyes possessing excellent wetting-out power are prepared by adding thereto small quantities of selected fractions of naphthenic acids, whereby the selection is so made that the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of alkali in the lye}}$$

must be a number between 15 and 25. This mathematical expression means that for lyes of lower concentration fractions of naphthenic acids with a low acid number are used, whereas for concentrated lyes naphthenic acids possessing a high acid number will be employed. Instead of the expression acid number it is also possible to say molecular weight, as a low acid number of a fraction indicates high molecular naphthenic acids, and a high acid number indicates low molecular acids. If the acid number is adapted to the concentration of the lye by following the above mathematical rule, the naphthenic acid fraction will generally be clearly soluble in the lye and impart thereto a powerful wetting-out and penetrating action for raw cellulosic fibres. Such a lye will then be of great advantage for the treatment of cellulosic material, for instance for the mercerisation of raw unbowked cotton or the alkalisation of raw paper pulp in the manufacture of rayon.

The acid number of naphthenic acids varies between 250 and 500 and if the above rule is followed, it will be clear that for sodium hydroxide lyes of 30° Bé. and upwards, naphthenic acid fractions possessing the acid number 380 and upwards will be preferably used. For caustic soda lyes of about 26–30° Bé. fractions with the acid number of about 360–380 are preferable. For more dilute lyes say of 22–26° Bé. fractions with the acid number of about 320–360 are suitable. If dilute lyes, say of 18–22° Bé., are used, then the corresponding acid number of the naphthenic acid fractions will be of 250–320.

It has further been observed that the wetting-out power of naphthenic acids can be increased if the above quotient increases in value by adding thereto a small amount of amino- or ether alcohols. In the case the quotient sinks, then the activity of the naphthenic acids can be increased by adding thereto a certain amount of emulsifying agents of a nonphenolic character.

This means that when naphthenic acid fractions of low molecular weight are used in rather dilute alkaline lyes, they obtain the property of emulsifying therein substances like amino- or ether alcohols, which then increase the wetting-out power of alkaline lyes. For instance if naphthenic acid fractions with the acid number 380 and upwards are used in lyes of say 22–28° Bé., it is indicated to add to the naphthenic acids a small amount of amino- or ether alcohols and to use such mixtures as wetting agent, which will then increase the wetting-out properties of alkaline lyes much stronger than if the naphthenic acids fractions are used alone.

In case that naphthenic acids of high molecular weight or of low acid number are used in concentrated alkaline lyes, it happens that they are no more completely soluble therein and instead of clear solutions, muddy alkaline lyes are obtained. In such a case it has been observed that it is possible to increase the wetting-out power of naphthenic acid and to prepare clear soluble mixtures by adding to the naphthenic acid fraction a certain amount of emulsifying agents of generally acid character or belonging to the glucoside type containing at least four aliphatic hydroxy groups. For instance if a naphthenic acid fraction with the acid number 384 is used alone in lyes of 30–34° Bé., a muddy lye is obtained because the naphthenic acids are no more clearly soluble in such lyes. But if to such naphthenic acids a certain amount of an emulsifying agent like butylsulphate is added, then the mixtures thereby obtained become clearly soluble in lyes of such concentration and impart thereto a very powerful wetting-out action.

As ether alcohols saturated and unsaturated compounds of the aliphatic, cycloaliphatic, araliphatic and heterocyclic series containing besides

an ether linkage at least one aliphatic hydroxy group, such as the ethers of glycol, glycerine and polyvalent alcohols, the acetals derived from polyvalent alcohols and ketones or aldehydes can be used. As amino alcohols compounds containing one or more nitrogen atoms and one or more oxalkyl groups in the molecule are suitable for improving the wetting-out properties of the fractions of naphthenic acids. In case that the use of an emulsifying agent is indicated, derivatives are used which belong to the class of sulphonic acids of alkylated aromatic compounds, aliphatic and heterocyclic sulphonic acids with at least three carbon atoms in the molecule, the sulphuric esters of aliphatic alcohols with 2 to 12 carbon atoms possessing straight or ramified carbon chains, the sulphuric acid esters of ether- and amino alcohols, aliphatic saturated or unsaturated monocarboxylic acids with 3 to 12 carbon atoms and with straight ramified carbon chains, which chains can eventually contain oxygen bridges; such acids are for example isobutyric acid, isovalerianic acid, isocapronic acid, isobutylacetic acid, isoamyl acetic acid, methylisobutyl acetic acid, methylisoamyl acetic acid, ethylpropyl acetic acid, dipropyl acetic acid, 1:3-dimethyl valerianic acid, 3-methyl capronic acid, 1:3-dimethyl capronic acid, 3-methyl-capryl acid etc. (see British Patent No. 414,485), the glycosido-compounds obtainable from sugars and aliphatic alcohols or ether alcohols.

One object of the present invention is therefore a process for improving the wetting-out power of alkaline lyes of a concentration superior to 18° Bé. by adding thereto fractions of naphthenic acid selected in such a manner that the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of alkali in the lye}}$$

is a number between 15 and 25.

Another object of the present invention is a process for improving the wetting-out action of alkaline lyes by adding to concentrated lyes naphthenic acid fractions with a high acid number, and to more dilute lyes, fractions with a lower acid number.

Still another object of the present invention are the improved alkaline solutions of 18° Bé. and more containing suitable fractions of naphthenic acids.

Still another object of the present invention is the process for improving the wetting-out action of alkaline lyes by adding thereto mixtures of naphthenic acid fractions with amino- or ether alcohols in the case that the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of alkali in the lye}}$$

is a number greater than 25.

Still another object of the present invention is the process for improving the wetting-out action of alkaline lyes by adding thereto mixtures of naphthenic acid fractions with emulsifying agents of an acid character when the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of alkali in the lye}}$$

is a number lower than 15.

Still another object of the present invention are the alkaline lyes of 18° Bé. and more containing suitable fractions of naphthenic acid in mixture with amino- or ether alcohols or in mixture with emulsifying agents of an acid character and the process of treating cellulosic material, especially the mercerizing process of cellulosic fibres with the said lyes.

The following first table and examples show how the present invention can practically be carried out, the parts being by weight, or where especially indicated by volume:

Table I

1	2	3	4	5	6	7	8	9
Degrees			*Degrees*	*Cc.*	*Percent*	*Percent*	*Percent*	
95–130	394	25.5	32	10	4.6	11.0	16.4	15.45
95–130	394	24.5	31	10	8.0	16.4	20.8	16.1
95–130	394	23.5	30	10	9.2	17.0	20.8	16.76
95–130	394	21.5	28	10	9.3	16.5	19.4	18.3
95–130	394	18.7	25	10	9.3	14.7	16.7	21.07
130–140 American origin	384	23.5	30	7.5	6.3	14.2	19.2	16.34
100–130	389	23.5	30	5			21.0	16.55
130–140	384	22.5	29	7.5	11.7	19.2	21.6	17.0
130–140	384	21.5	28	7.5	13.0	19.5	21.6	17.86
130–140 Roumanian origin	358	19.65	26	5	13.4	19.6	21.6	18.17
130–140 American origin	384	18.7	25	5	9.2	15.2	17.0	20.53
130–140 American origin	384	18.7	25	7.5	11.4	17.0	18.6	20.53
140–150	356	18.7	25	3	10.0	15.4	17.7	
140–150	356	18.7	25	5	14.9	20.3	22.0	19.0
140–150	356	18.7	25	7.5	17.5	22.0	23.1	
148–162	325.5	16.0	22	7.5	15.6	18.7	19.7	20.34
148–162	325.5	16.0	20	7.5	9.8	12.4	13.3	22.6

Column 1 of this table gives the boiling point of the naphthenic acid fraction.

Column 2 of this table gives the acid number of the naphthenic acid fraction.

Column 3 of this table gives the content of free alkali in the lye.

Column 4 of this table gives the concentration of the lye in ° Bé.

Column 5 of this table gives the addition of naphthenic acid in cc. per liter lye.

Column 6 of this table gives the shrinkage of raw cotton yarn after 5 seconds.

Column 7 of this table gives the shrinkage of raw cotton yarn after 10 seconds.

Column 8 of this table gives the shrinkage of raw cotton yarn after 15 seconds.

Column 9 of this table gives the quotient.

The following second table shows the action, in lyes of different concentration, of mixtures of a naphthenic acid fraction of the acid number 384 and boiling point 130–140° C. with other compounds increasing its wetting-out properties in comparison to the action of the naphthenic acid fraction itself.

Table II

1	2	3	4	5	6	7
Cc.	*Cc.*	*Degrees*			*Per cent*	
7.5	0	34	27.65	13.91	0.6	Muddy.
7.5	10	34	27.65	13.91	11.4	Clear.
7.5	0	32	25.5	15.06	2.0	Muddy.
7.5	8	32	25.5	15.06	18.6	Clear.
7.5	0	30	23.5	16.34	19.2	Little muddy.
7.5	2.5	30	23.5	16.34	23.3	Clear.
7.5	0	29	22.5	17.0	21.6	Clear.
7.5	2.5	29	22.5	17.0	21.4	Do.
7.5	0	28	21.55	17.86	21.6	Clear.
7.5	2.5	28	21.55	17.86	20.8	Do.

Column 1 of this table indicates the quantity of naphthenic acid added to 1 liter lye.

Column 2 of this table indicates the quantity of 55% aqueous solution of the sodium salt of the n-butylsulphuric acid.

Column 3 of this table indicates the concentration of the lye.

Column 4 of this table indicates the content of the lye on free alkali in %.

Column 5 of this table indicates the quotient.

Column 6 of this table indicates the shrinkage of a raw cotton yarn after 15 seconds treatment.

Column 7 of this table indicates the nature of the lye.

The following Table III shows the action of the same naphthenic acid fraction as above in mixture with the acetals obtained from glycerine and technical methylcyclohexanones.

Table III

1	2	3	4	5	6	7	8
Cc.		*Cc.*	*Degrees*			*Per-cent*	
------	95:5	7.5	29	22.5	17.0	23.4	Little muddy.
------	95:5	7.5	28	21.55	17.86	23.3	Clear.
7.5	0 cc.	0	25	18.71	20.53	18.6	Clear.
------	90:10	7.5	25	18.71	20.53	23.6	Do.
7.5	0 cc.	0	22	16.0	24.0	11.7	Clear.
------	80:20	7.5	22	16.0	24.0	19.0	Do.
7.5	0 cc.	0	20	14.3	26.8	6.2	Clear.
------	80:20	7.5	20	14.3	26.8	11.2	Do.

Column 1 of this table indicates the quantity of naphthenic acid added to the lye.

Column 2 of this table indicates the ratio of mixture of naphthenic acids with the acetals.

Column 3 of this table indicates the quantity of the mixture added to the lye.

Column 4 of this table indicates the concentration of the lye.

Column 5 of this table indicates the content of the lye on free alkali in %.

Column 6 of this table indicates the quotient.

Column 7 of this table indicates the shrinkage of a raw cotton yarn after 15 seconds treatment.

Column 8 of this table indicates the nature of the lye.

Lyes possessing excellent wetting-out power may further be prepared by using following mixtures:

1. Mix 5 cc. of naphthenic acids of acid number 356 with 7 cc. of a 49% aqueous solution of the sodium salt of the butoxyethane sulphonic acid

$$(CH_3—CH_2—CH_2—CH_2—O—CH_2—CH_2—SO_3Na)$$

and add this mixture to a liter of lye of 28° Bé. The lye thus obtained is clear and the shrinkage of a raw cotton yarn after 15 seconds immersion reaches 23.8%.

2. Mix 4.5 cc. of raw naphthenic acids of acid number 291 with 10.5 cc. of isovalerianic acid and add this mixture to a liter of lye of 30° Bé. Instead of isovalerianic acid, methylisobutyl acetic acid can be used, and mixed with naphthenic acid of acid number 331.

3. Mix 2.31 parts of naphthenic acids of acid number 359 with 5.39 parts of isoamyl glucoside and add this mixture to a liter of lye of 35° Bé.

4. Add to a liter of lye of 35° Bé. a mixture of 5 cc. of naphthenic acids of acid number 389 with 12 cc. of n-propylsulphate. Clear lye with good wetting action will be obtained.

5. Add to a liter of lye of 23° Bé. a mixture of 9 cc. of naphthenic acids of acid number 356 with 1 cc. of di-(oxethyl)-n-butylamine. Clear lye with good wetting-out action will be obtained.

By replacing the above amine by monooxethyl-isoamylamine or by di-(oxethyl)-isoamylamine, active wetting-out agents will be obtained.

6. Add to a liter of lye of 25° Bé. 5 cc. of a mixture consisting of

92 parts of naphthenic acids with acid number 384 and
8 parts of diethyleneglycolmonobutylether or of
95 parts of naphthenic acids and
5 parts of glycerine-α-isoamylether.

Clear lyes with good wetting-out action will be obtained.

7. Add to a liter of lye of 32° Bé. a mixture of 5 cc. of naphthenic acids of acid number 384 with 3.5 cc. of the concentrated aqueous solution of the sodium salt of a high sulphonated ricinoleic acid. Clear and stable lyes will be obtained.

What I claim is:

1. The phenol-free alkaline lyes of 18° Bé. and more, possessing good wetting out properties and containing a wetting-capacity increasing agent consisting of such fractions of naphthenic acids that the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

2. The phenol-free alkaline lyes of 30° Bé. and more, possessing good wetting-out properties and containing a wetting capacity increasing agent consisting of such fractions of naphthenic acids, the acid number of which is 380 and more and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

3. The phenol-free alkaline lyes of 26–30° Bé., possessing good wetting-out properties and containing a wetting capacity increasing agent consisting of such fractions of naphthenic acids, the acid number of which is 360–380 and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

4. The phenol-free alkaline lyes of 18–26° Bé., possessing good wetting-out properties and containing a wetting capacity increasing agent consisting of such fractions of naphthenic acids, the acid number of which is 250–360 and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

5. A process for the alkaline treatment of cellulosic material, comprising subjecting the

cellulosic material to a treatment with a phenol-free alkaline lye of 18° Bé. and more, containing a wetting capacity increasing agent consisting of such fractions of naphthenic acids that the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

6. A process for the alkaline treatment of cellulosic material, comprising subjecting the cellulosic material to a treatment with phenol-free alkaline lyes of 30° Bé. and more, containa wetting capacity increasing agent consisting of fractions of naphthenic acids, the acid number of which is 380 and more and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

7. A process for the alkaline treatment of cellulosic material, comprising subjecting the cellulosic material to a treatment with phenol-free alkaline lyes of 26–30° Bé., containing a wetting capacity increasing agent consisting of fractions of naphthenic acids, the acid number of which is 360–380 and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

8. A process for the alkaline treatment of cellulosic material, comprising subjecting the cellulosic material to a treatment with phenol-free alkaline lyes of 18–26° Bé., containing a wetting capacity increasing agent consisting of fractions of naphthenic acids, the acid number of which is 250–360 and the quotient

$$\frac{\text{acid number of the naphthenic acid fraction}}{\text{content in percent of the alkali in the lye}}$$

is a number between 15–25.

HEINRICH LIER.