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COAGULATION OF EMULSIONS OF ORGANIC FILM-FORMING MATERIALS

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The present invention relates to a process for coagulating organic film-forming materials from aqueous emulsions thereof by heat.

It is known that natural latex can be rendered sensible towards heat by the incorporation therewith of mild coagulating agents. Such auxiliary agents are, for instance, ammonium or alkali metal salts either alone or in the presence of zinc salts. Natural latex having dissolved therein such agents is stable in the cold and coagulates on heating. Owing to such properties, such latices are made use of for the preparation of dipped goods, films, spongy rubber, rubber threads and the like. Earth alkali metal salts, for instance calcium salts, have also been proposed for the purpose in question. However, such agents suffer from the disadvantage that the lower and the upper limit of the permissible amount thereof must be carefully controlled if a premature coagulation is to be avoided and, on the other hand, a satisfactory coagulating effect is to be achieved in the heat. Generally spoken, there is still a lack of heat-sensibilizing agents which allow one to store such latices for an indefinite period of time without inducing the danger of a premature coagulation and, on the other hand, secure a good coagulation effect in the heat. As to the emulsions of other organic film-forming materials, for instance, those prepared by the emulsion polymerization of butadienes-1.3 or of mixtures of butadienes and other copolymerizable compounds or from polymerizable vinyl compounds or mixtures thereof, up to the present no satisfactory heat-sensibilizing process has been developed at all. Thus, alkali or ammonium salts if incorporated within such emulsions either exert no coagulating effect at all or, if employed in a higher concentration, result in a premature coagulation at ordinary temperature.

It is, therefore, the object of our present invention to do away with these disadvantages and to develop a heat-sensibilizing process for emulsions of organic film-forming materials which secures a better stability of the emulsions in the cold without impairing their capability of being coagulated in the heat. Another object of our invention resides in that emulsions of other film-forming materials than natural rubber are rendered suitable for the purpose in question. Still another object of our invention is to be seen in the preparation of molded articles, dipped goods, spongy rubber, rubber threads and the like from such emulsions.

With these and other objects in view our invention in its broadest aspect comprises dissolving a water-soluble, highly active coagulating agent within an aqueous emulsion of an organic film-forming material having incorporated therewith a water-soluble product of the interaction of a 1.2-alkylene oxide upon a hydroxy compound, an amine or carboxylic acid, which have an aliphatic radical of at least 8 carbon atoms, and heating the emulsion to a temperature at which the said alkylene oxide reaction product becomes insoluble in water. The emulsion and the highly active coagulating agent must be chosen in such a manner that in the absence of the said alkylene oxide reaction product the former would be precipitated by the latter. In general, such emulsions are chosen as are capable of being coagulated by calcium chloride. The invention is based upon the discovery that the condensation products of the character described exert an excellent stabilizing effect upon such aqueous emulsions even towards highly active coagulating agents and that this stabilizing action gradually decreases with an increase of temperature. This effect is probably due to the fact that the said alkylene oxide-condensation products are better soluble in cold water than in hot water. Emulsions containing such alkylene oxide-condensation products and highly active coagulating agents can be stored at room temperature for a practically indefinite period of time without any premature coagulation. This is also true in the case of rubber latex or of emulsions of synthetic rubber-like materials having incorporated therewith filling materials, vulcanizing agents, vulcanization accelerators and the like. The viscosity and workability of the emulsions is not materially increased by the dissolution therein of the said auxiliary agents. In consequence thereof, our new process is very suitable for the preparation of molded articles, dipped goods, spongy rubber, rubber threads and the like. This is true in the case of natural latex as well as in the case of aqueous emulsions of other organic film-forming materials most of which could not be worked according to such heat-sensibilizing processes up to the present.

Turning now to our new invention in detail, we prefer ethylene oxide-condensation products though products derived from other 1.2-alkylene oxides such as glycide are by no means excluded. The amount of the 1.2-alkylene oxide must be such as to impart solubility in water to the water-insoluble hydroxy compounds, carboxylic acids or amines. Besides pure aliphatic hydroxy- or amino compounds or pure aliphatic carboxylic acids, there can also be employed the corresponding alkylated aromatic compounds such as isododecylphenol. A preferred higher aliphatic compound is oleyl alcohol, the preferred condensation product being obtainable from 1 mol of oleyl alcohol and 20 mols of ethylene oxide. Products of the interaction of alkylene oxides and amines or carboxylic acids yield more homogeneous coagulates whereas the stabilizing action is the best in the case of the alcohol condensation

products. As a matter of fact, mixtures of various stabilizing agents of the character described can also be employed.—Besides natural rubber there can be employed emulsions of every kind of organic film-forming materials. The term "film-forming" is intended to cover all such materials as are capable of forming on coagulation a coherent film, either porous or homogeneous. Such compounds are, for instance, the latex-like products of the emulsion polymerization of butadiene hydrocarbons or halogen containing butadienes or of mixtures of such butadienes and other copolymerizable compounds. Furthermore, there can be employed emulsions of other non rubber-like polymerization products such as polyvinyl esters, polystyrene, polyacrylic acid esters, polyisobutylene and of mixed polymerizates of such compounds.—As highly active coagulating agents, we prefer to employ salts of polyvalent metals, for instance, water-soluble mineral acid salts of earth alkali metals such as calcium or of aluminium. Furthermore, there can be employed strong acids such as hydrogen chloride.—As a matter of fact, the emulsions may contain various other modifying agents, such as softeners, filling materials, pigments and the like and also (in the case of vulcanizable materials) vulcanizing agents, vulcanization accelerators; anti-perishing agents and the like.

The emulsion polymerizates of the character defined in the foregoing paragraph must be prepared in the presence of protective colloids or of an emulsifying agent. As the alkylene oxide condensation products represent excellent emulsifying agents, these emulsions may contain such condensation products from the very beginning. It is pointed out that in this case the additional incorporation within the emulsion of such alkylene oxide condensation products can be dispensed with.

Our invention is furthermore illustrated by the following examples, without, however, being restricted thereto, the parts being by weight, unless otherwise stated.

Example 1

156.0 ccms of a 32% emulsion of a mixed polymerizate from butadiene-1.3 and acrylic acid nitrile (75:25) are mixed while stirring with a 20% aqueous solution of an emulsifying agent which has been prepared from 1 mol of oleyl alcohol and 20 mols of ethylene oxide, and with a calcium chloride solution as precipitating agent. The following table illustrates the influence which is exerted upon the temperature of coagulation by the concentration of the stabilizing agent and of the calcium chloride, the temperature being being raised for about 15°C per minute:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $CaCl_2$-solution	Coagulation-temperature
		Degrees
7.5	10	45
10.0	10	62
12.5	10	70
15.0	10	79
7.5	20	37
10.0	20	50
12.5	20	65
15.0	20	76

Similar results are obtained by the use of ethylene oxide-octyl alcohol-condensation products or of condensation products prepared from glycide.

Example 2

In case the calcium chloride of example 1 is replaced by aluminium chloride, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $AlCl_3$-solution	Coagulation-temperature
		Degrees
10.0	10	45
12.5	10	55
15.0	10	65

Example 3

In case the emulsion of example 1 is replaced by 187 ccms of a 26.6% emulsion of a mixed polymerizate from butadiene and acrylic acid nitrile (50:50), the following figures have been obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $CaCl_2$-solution	Coagulation-temperature
		Degrees
10.0	20	42
12.0	20	56
15.0	20	63

Example 4

In case in example 3 $AlCl_3$ is used as precipitating agent, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $AlCl_3$-solution	Coagulation-temperature
		Degrees
10.0	10	25
12.5	10	36
15.0	10	45

Example 5

In case in example 1 172 ccms of a 29% emulsion of a mixed polymerizate from butadiene and styrene (75:25) are used as latex, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $CaCl_2$-solution	Coagulation-temperature
		Degrees
7.5	10	39
10.0	10	50
12.5	10	63
15.0	10	72
10.0	20	50
12.5	20	62
15.0	20	72

Example 6

In case in example 5 $AlCl_3$ is used as precipitating agent, the following figures are obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 20% $AlCl_3$-solution	Coagulation-temperature
		Degrees
12.5	10	44
15.0	10	56

Example 7

In case in example 1 100 ccms of a 50% natural latex are employed, the following figures are found:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 10% $CaCl_2$-solution	Coagulation-temperature
		Degrees
1.5	20	63
2.5	20	63
5.0	20	63
7.5	20	67
10.0	20	70
12.5	20	75
15.0	20	77

Example 8

15 parts of a 20% solution of a condensation product of isooctylphenol with ethylene oxide and 40 parts of a 20% solution of calcium chloride are added to 330 parts of a 30% aqueous dispersion of a mixed polymerizate from butadiene and acrylic acid nitrile containing as dispersing agent sodium isobutylnaphthalenesulfonate. When warmed, this latex mixture coagulates completely. A mold which is kept at a temperature of about 100°C, when dipped into this mixture, is covered in the course of 1 minute with a film having a strength of about 0.5 mms.

Example 9

To a latex mixture containing besides vulcanization additions also filling and plastifying agents and having the following composition:

	Parts
A mixed polymerizate from butadiene and acrylic acid nitrile in the form of a 30% latex	100.00
Dibenzyl ether	2.50
A condensation product of 1 mol of oleic acid with 20 mols of ethylene oxide	1.00
A 20% aqueous solution of a condensation product of ethylene oxide with oleyl alcohol	18.50
A 85% sulfur	3.00
Zinc oxide	5.00
Caolin	10.00
Piperidine pentamethylenedithiocarbaminate	0.30
Hexahydroaniline cyclohexylethyldithiocarbaminate	0.30
A 5% solution of the sodium salt of a condensation product of naphthalene sulfonic acid with formaldehyde	40.00

are added 40 parts of a 10% calcium chloride solution. The mixture which, in the absence of calcium chloride, is stable to the influence of heat, coagulates after the addition of calcium chloride at about 65°C. The mixture may be stored at room temperature for many days. When dipping hot molds into the latex mixture or when heating the latex mixture in molds, coatings of a considerable strength are obtained. When extruding the emulsion through a heated nozzle, a uniform and smooth rubber thread is obtained.

Example 10

In case in example 1 aluminium chloride is employed as emulsifying agent, the following figures have been obtained:

Ccms of a 20% solution of the emulsifying agent	Ccms of a 10% $AlCl_3$-solution	Coagulation-temperature
		Degrees
7.5	10	56
7.5	7.5	72
7.5	5	90

Example 11

80 ccms of a 60% natural latex are mixed with a 10% aqueous solution of a condensation product of 1 mol of stearic acid and 13 mols of ethylene oxide while stirring and with a $CaCl_2$-solution as precipitating agent.

Ccms of a 10% solution of the emulsifying agent	Ccms of a 10% $CaCl_2$-solution	Coagulation-temperature
		Degrees
2.5	5	33
5.0	5	30
7.5	5	28
10.0	5	30
12.5	5	32

Example 12

In case in example 11 78 ccms of a 32% emulsion of a mixed polymerizate from butadiene and acrylic acid nitrile (75:25) are used as latex, the following figures are obtained:

Ccms of a 10% solution of the emulsifying agent of example 11	Ccms of a 10% $CaCl_2$-solution	Coagulation-temperature
		Degrees
10.0	5	50
12.5	5	55
15.0	5	62

Example 13

40 ccms of a 60% natural latex are mixed with a solution consisting of 40 parts of a 10% solution of a condensation product of 1 mol of stearic acid with 13 mols of ethylene oxide and 10 parts of a 20% solution of a condensation product of 1 mol of oleyl alcohol and 20 mols of ethylene oxide.

Ccms of the above-mentioned solution of the emulsifying agent.	Ccms of a 10% $CaCl_2$-solution	Coagulation-temperature
		Degrees
1.25	5	32
2.50	5	52
5.00	5	63
7.50	5	62
10.00	5	60

Example 14

In case in example 13 a mixture of a 60% natural latex and a 32% emulsion of butadiene and

acrylic acid nitrile (75:25) is used as latex, the following figures are to be formed:

Ccms of the solution of the emulsifying agent of example 13	Ccms of a 60% natural latex	Ccms of the 32% mixed polymerizate latex	Ccms of a 10% $CaCl_2$ solution	Coagulation-temperature
				Degrees
10	67	31	10	46
10	50	62	10	42
15	33	93	10	50
15	16.5	124	10	40

In this case, especially smooth films are obtained.

Example 15

78 parts of a 32.2% latex of a mixed polymerizate from butadiene and acrylic acid nitrile in the proportion 75:25 are mixed with the solution of a stearylamine-ethylene oxide-condensation product and calcium chloride in the quantities as indicated in the following table, whereupon the following temperatures are obtained:

Parts of a 10% solution of the stabilizing agent	Parts of a 10% solution of the coagulating agent	Coagulation-temperature
		Degrees
15	5	65
17.5	5	72
20	5	77

Example 16

50 parts of a butadiene-acrylic acid nitrile-mixed polymerizate (in the proportion 6:4) in the form of a 30% latex,
50 parts of natural rubber in the form of a 60% latex are heated with
3 parts of colloid sulfur,
10 parts of active zinc oxide,
0.6 parts of zinc phenylethyldithiocarbaminate as accelerator, the three last-mentioned components being dispersed in
10 parts of a 5% solution of the sodium salt of a condensation product of naphthalenesulfonic acid and formaldehyde.
25 parts of the mixture of emulsifying agents according to example 13 and
30 parts of a 10% calcium chloride solution are added thereto.

When dipping hot molds into this sensibilized mixture, strong vulcanizable films are obtained.

Example 17

50 parts of the mixed polymerizate of example 16 in the form of a 30% latex and
50 parts of natural rubber in the form of a 60% latex are mixed with a dispersion of sulfur, zinc oxide and the accelerator of example 16.
20 parts of the solution of an emulsifying agent consisting of 40 parts of a 20% solution of a condensation product of 1 mol of stearylamine and about 5 mols of ethylene oxide and 10 parts of a 20% solution of a condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide are added thereto. To this mixture,
50 parts of a 10% calcium chloride solution are added.

When dipping hot molds into this mixture, strong films are obtained which, after washing with water and drying, are vulcanized.

Example 18

As emulsion there have been used: 80 parts of a 25% emulsion of a mixed polymerizate of 66% acrylic acid methylester, 22% vinylisobutylether and 12% styrene. Upon the addition of stabilizer and of calcium chloride the following figures have been obtained:

Parts of a 20% aqueous solution of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of 10% $CaCl_2$	Coagulation-temperature
		Degrees
1	10	45
2	10	70
4	10	83
6	10	86
8	10	89
10	10	90

Example 19

In case 80 parts of a 30% polystyrene emulsion are used, the following results have been obtained:

Parts of a 20% aqueous emulsion of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of a 10% $CaCl_2$ solution	Coagulation-temperature
		Degrees
5.0	10	45
6.0	10	55
6.5	10	85

Example 20

In case a polystyrene emulsion is employed for the manufacture of molded articles, plastifying agents are suitably added to the mixtures to be sensibilized. These plastifying agents have the effect that the coagulate does not form a crumbly mass, but a homogeneous product. In the table mentioned below, dibutylphthalate is employed by way of example, a 20% solution of the condensation product of 1 mol of oleylalcohol with 20 mols of ethylene oxide being used for emulsifying the same and for stabilizing the mixture.

Parts of a 20% aqueous solution of the condensation product of 1 mol of oleyl alcohol with 20 mols of ethylene oxide	Parts of dibutyl-phthalate	Parts of a 10% $CaCl_2$ solution	Coagulation temp.
			Degrees
5	2.5	10	85
5	5.0	10	85
5	10.0	10	85

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