Jan. 17, 1950 J. N. STREET 2,495,147

COAGULATION PROCESS AND APPARATUS

Filed June 18, 1946 2 Sheets-Sheet 1

Fig. 1

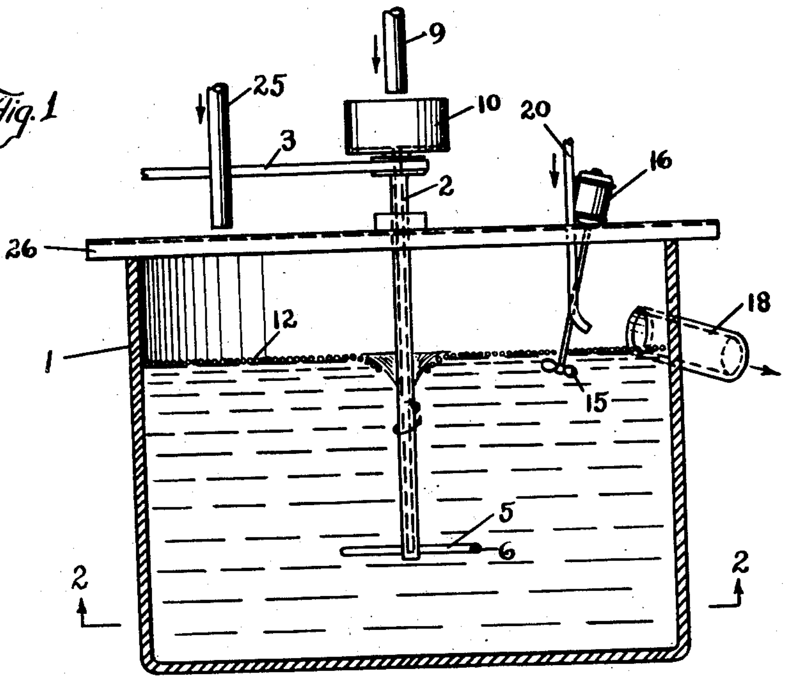

Fig. 2

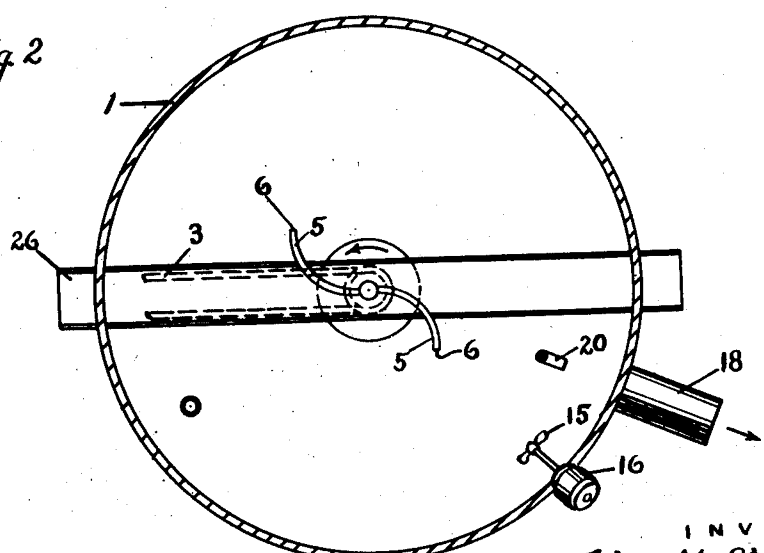

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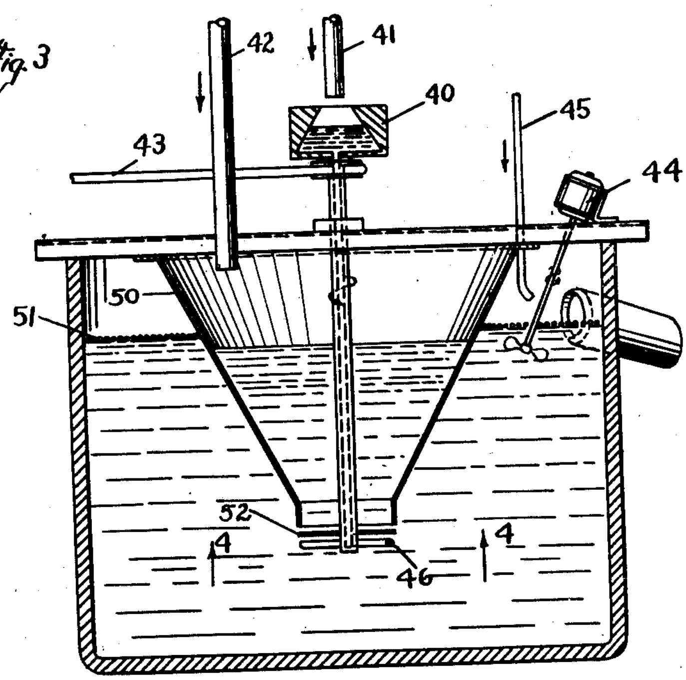
Fig. 3



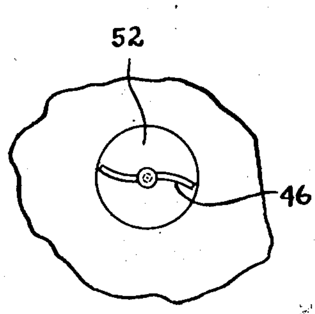


Fig. 4

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Patented Jan. 17, 1950

2,495,147

UNITED STATES PATENT OFFICE

2,495,147

COAGULATION PROCESS AND APPARATUS

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Application June 18, 1946, Serial No. 677,588

2 Claims. (Cl. 260—96)

This invention relates to the coagulation of dispersions of rubber-like and resinous materials. More particularly, it relates to the coagulation of such materials in the form of a crumb. The invention includes the process and preferred apparatus for carrying out the process.

Prior to this invention it has been customary to coagulate rubber-like and resinous materials from a dispersion of the same by forming a single coagulated mass of all the coagulable material in the dispersion. Because the mass of coagulum is rubber-like or resinous, it has been difficult or impossible to separate uncoagulated dispersion and coagulant from the coagulum because some of it is enclosed in pockets in the coagulum. Furthermore, it has been difficult or impossible to wash the coagulum free of such aqueous impurities and to dry the mass.

According to this invention the coagulum is obtained as a crumb; i. e., as discrete particles which are easily filtered and washed and thus separated from aqueous impurities. These particles are quickly dried and are easily handled in further processing. The crumb is obtained by introducing the dispersion of resinous or rubber-like material under the surface of a bath of coagulant. The dispersion is brought into contact with the coagulant as discrete droplets so that the coagulum is produced as crumb. A continuous stream of the dispersion may be used which is broken up into droplets as it comes into contact with the coagulant, or prior thereto. The stream of dispersion may be aspirated with air or other gas if desired. The separated portions of the stream are coagulated out of contact with one another while surrounded by coagulant, and the coagulum obtained is in the form of separated particles or crumb. The size of the crumb particles may vary from the size of sand to the size of a pea, for example. If the coagulum has a gravity greater than the coagulant solution, the crumb will sink to the bottom of the vessel in which the coagulation is carried out. If it is of lighter gravity, it will rise to the top. The invention relates more particularly to the production of crumb which rises to the top and includes maintaining the particles of crumb in a nonagglomerated or segregated condition and the removal of them from the top of the coagulant bath. Thus, the process may advantageously be carried out on a continuous basis with removal of the crumb from the bath as it is formed. Alternatively, the bath may be agitated sufficiently to produce a uniform slurry of the crumb and coagulant which may be removed from the

top or bottom or any other convenient part of the bath, and the operation may be continuous if desired.

A preferred type of apparatus for carrying out the process uses a hollow agitator with hollow agitating arms with an orifice at or near the end of each through which the dispersion is introduced into the coagulating bath. If the crumb is allowed to rise to the surface of the bath and it is tacky (a valuable characteristic in synthetic rubbers), agitation at the surface, preferably just prior to the removal of the crumb from the bath, maintains the particles of the crumb in a segregated condition and facilitates its removal from the bath.

The crumb is advantageously removed from the surface of the bath soon after it is formed. If the latex is introduced through the arms of a revolving agitator, or other agitator means is used so that a swirling motion is imparted to the entire coagulant bath; and if the gravity of the crumb is so low that it rises to the surface of the coagulant (which is the case with most rubber-like materials and many resinous materials), the crumb can readily be collected from the surface of the bath by providing an overflow outlet and suitable baffles—e. g., screen baffles which do not impede the flow of the liquid—or by directing a jet of air or other gas or a liquid against the crumb to direct it to the overflow outlet. Any suitable means for accomplishing this may be employed. A mechanical sweep may be used satisfactorily even though the body of liquid is not swirling.

The invention is applicable to the coagulation of synthetic rubbers obtained as a dispersion by emulsion polymerization or copolymerization. The rubber may be a polymer of butadiene or isoprene. It may be a copolymer of (1) a conjugated diene—for example, butadiene, isoprene, 2-cyanobutadiene, cyclopentadiene, piperylene, dimethylbutadiene, 2-methyl-1,3-pentadiene, etc.—and either (2a) a vinyl aromatic compound—for example, styrene, alpha-methylstyrene, nuclear-substituted styrenes, dichlorostyrene, vinylnaphthalene, vinylbiphenyl, vinylcarbazole, 2-vinyl-5-ethylpyridine, 2-ethyl-5-vinylpyridine, etc.—or (2b) a monomer having the formula

$$CH_2{=}C(R)-X$$

when R is hydrogen, methyl, ethyl, propyl or chlorine and X is —CN, —$CONH_2$, —COR′ or —COOR′ and R′ is an alkyl group which contains from one to no more than about five carbon atoms. The invention is not limited to the coagulation of dispersions of such rubber-like materials but includes also the coagulation of dispersions of other rubber-like materials, regardless of how the dispersions are obtained. Dispersions of resinous materials similarly produced by emulsion polymerization or copolymerization, such as, for example, the polymerization of styrene, vinyl esters such as vinyl chloride, etc., ethylene, tetrafluorethylene, esters of acrylic acid and derivatives thereof such as methyl methacrylate, etc., vinylpyridine, etc., and the copolymerization of vinyl chloride and vinylidine chloride, butadiene and styrene in suitable proportions to produce a resin, etc., or dispersion of resinous material which may be obtained in any other manner, may, likewise, advantageously be coagulated by the process of this invention. The invention, likewise, includes the coagulation of natural rubber latices. Such dispersions are mentioned as illustrative and not in a limiting sense.

The invention applies generally to coagulation with any aqueous coagulant which may, for example, be a water solution of an acid (for example, sulfuric acid, hydrochloric acid or acetic acid, etc.) or a water solution of a salt (for example, sodium chloride, magnesium sulfate, calcium chloride or aluminum sulfate, etc.) or other aqueous coagulant. The process is most advantageously employed with a system in which the coagulant acts rapidly.

Ordinary precautions will be used, as, for example, operating in the absence of iron salts in the treatment of rubber-like copolymers of butadiene and styrene.

The invention will be further described in connection with the accompanying drawings, in which:

Fig. 1 is an elevation in section of apparatus for coagulation;

Fig. 2 is an upward view on the line 2—2 of Fig. 1;

Fig. 3 is an elevation in section of modified apparatus; and

Fig. 4 is an upward view on the line 4—4 of Fig. 2.

In the drawings the coagulation tank 1 is equipped with an agitator 2 driven by a belt 3 from a motor (not shown). The agitator is provided near the bottom with the arms 5 which in the drawing curve backwardly although this is not necessary. The shaft 2 of the agitator and the arms 5 are hollow. The end 6 of each arm is provided with a small orifice. The size, shape, and position of the orifice influence the rate of introduction of the dispersion and the size of the coagulated particles obtained. The orifice faces away from the direction in which the arm is rotated. It may be located at the end of the arm, whether the arm extends radially from the shaft or in a curved line; or it may be located on the top, bottom or back side of the arm. A multiplicity of orifices may be provided in a single arm. The dispersion introduced through the feed line 9 collects in the feed tank 10 and is fed from the tank through the shaft 2 into the arms 5 and out through the orifices in the ends of the arms. As the shaft and arms are rotated, the dispersion is introduced under the surface of the coagulant in the tank in the form of either a continuous or a discontinuous stream, but due to the shear forces set up, the effect is to produce discrete particles. The centrifugal force set up by the rotation of the agitator and the pull of the coagulant on the orifices draws the dispersion through the agitator into the coagulant. Added pressure may be provided by maintaining the feed tank 10 under pressure.

As illustrated, the tank 10 rotates with the agitator. The centrifugal force of the liquid in the tank causes the liquid to build up against the lateral walls of the tank, and depending upon the speed of rotation and the amount of liquid within the tank, air may be drawn down through the shaft 2 so that the dispersion is aspirated as it is introduced into the coagulant. Whether aspirated or not, the dispersion is supplied in the form of a discontinuous stream. The droplets of the dispersion are coagulated as they leave the rotating orifices and before they have time to coalesce into a continuous body. If the gravity of the crumb produced is less than the gravity of the coagulant, the crumb particles rise to the surface of the tank and are indicated at 12.

If the crumb particles are tacky (and rubber-like particles usually are), it may be advantageous to break up any adherence between them just before removing them from the bath. The blades 15 of the agitator 16 do this by keeping the surface of the coagulant within the tank thoroughly agitated just ahead of the overflow pipe 18. Thus, the crumb particles flow through the overflow 18 in a disaggregated or segregated condition. To aid in the prompt removal of the crumb from the coagulant, a jet of air from pipe 20 is blown across the surface of the bath into the mouth of the overflow.

The whole body of coagulant swirls at a speed somewhat less than the rate of rotation of the agitator so that the surface of the body of the bath is continuously revolving. The arms may be streamlined, and baffles may be provided to dampen the swirling action. Soon after the crumb rises to the top of the bath, the swirling of the bath brings it into the agitated zone near the agitator 15, and any aggregations of the crumb are broken up. The jet of air from the pipe 20 directs the particles of crumb to the overflow outlet 18. Only a small amount of the crumb escapes the action of the air jet or other collection means and completes the circuit of the tank. Most of the crumb is removed from the coagulant bath soon after it is formed.

The mixture of crumb and mother liquor or coagulant which passes out through the overflow is easily separated by filtration or centrifuging, and the crumb particles are then readily washed. A portion or all of the coagulant collected may be returned to the coagulating tank through the coagulant feed pipe 25. The concentration of the coagulant in the feed is adjusted to maintain a desired coagulant concentration in the tank.

The channel 26 simply serves to support the agitator.

Improved equipment is shown in Figs. 3 and 4. Here the walls of the feed tank 40 are arched inwardly to prevent overflow of the latex. This reduces or eliminates the possibility of the dispersion being aspirated as it is fed under the surface of the coagulant. However, it permits a head of the dispersion to be built up, and this makes possible the introduction of the dispersion at a higher rate than is possible with the equipment illustrated in Fig. 1.

The dispersion feed pipe 41, the coagulant feed pipe 42, the drive belt 43, agitator 44, air jet 45, and agitator arms 46 are the same as in Figs. 1 and 2. The inverted cone 50 diverts the crumb particles 51 to the walls of the coagulating tank and prevents their collecting around the shaft of the agitator. The plate 52 directs the fresh coagulant from within the cone into the path of the droplets of the dispersion as they are released through the orifices in the ends of the arms 46. The centrifugal force generated by the swirling of the liquid outside of the cone 50 makes the level of the liquid outside of the cone higher than that inside, somewhat as indicated. By reducing the area of the surface of the liquid in which the crumb particles collect, the crumb particles are more easily subjected to the action of the blades of the agitator 44 and are more completely removed by the air jet 45.

Modifications in the design of the equipment may be made without departing from the scope of the invention. The dimensions of the coagulation tank and its shape may be altered. The number of agitator arms on the hollow agitator shaft may be varied. Other means for introducing the dispersion into the coagulating bath may be utilized. The proportions of the equipment may be varied. Although rotations of the agitator arms at speeds of 600 and 1200 R. P. M. and even as low as 100 or 200 R. P. M. have proved satisfactory, this may be varied, the length of the arm having a definite relation to the speed of rotation which might be desirable. Good results have been obtained with the agitator arms submerged a foot under the surface of the bath, but this may be varied. The speed of rotation of the agitator arms, their length, and the depth of their submergence are controlling factors in the pressure at which the dispersion is introduced. The concentration of the coagulant bath may vary. Concentrations of 1 and 4 per cent of aluminum sulfate have been used satisfactorily in the coagulation of dispersions of different rubber-like copolymers introduced into the coagulant at a depth of about 1 foot. The size and number of the orifices may be varied. Large volumes of dispersion may be passed through relatively small orifices when the speed of rotation of the agitator arms is high. Effective operation of the process is not dependent upon any swirling movement being imparted to the body of the coagulant. Thus, the process and design of the apparatus are subject to wide variations. Crumb of various rubber-like copolymers was satisfactorily produced in equipment such as illustrated in Figs. 3 and 4 with a metal tank 5½ feet in diameter, using a cone with a diameter of 28 inches at the surface and employing a jet for removing the crumb from the surface of the coagulant through the overflow outlet.

The following illustrates more particularly one operation and refers to a single arm although this may be duplicated any desired number of times in a single coagulating bath. The vessel may be of the general type illustrated in Fig. 1 or Fig. 3. To start, the vessel is charged about half full with a 1 per cent solution of alum in water. The shaft is rotated at 600 R. P. M. There is fed through the shaft the latex of a synthetic rubber (30 per cent solids, by weight) obtained by emulsion copolymerization of butadiene and acrylonitrile in the ratio of 60 parts of butadiene to 40 parts of acrylonitrile, or other ratio to produce a rubber-like copolymer. The shaft may, for example, have an opening $\frac{1}{16}$ inch in diameter throughout its length, but closed at the bottom end. Each arm may be about 3 inches long and be provided with an orifice $\frac{3}{32}$ inch in diameter at the end, the curvature of the arm being approximately that shown in Fig. 4.

The arm may, for example, be immersed 20 inches under the surface of the coagulant. The rubber will be coagulated as a fine crumb which will float to the surface and may be removed through a suitable outlet as described. The alum coagulant is replaced as used to maintain the ratio of the volume of the latex to the volume of the alum about 1 to 1 or somewhat less. Other ratios which vary materially from that suggested give satisfactory results, depending upon the concentration of the coagulant, the solids content of the dispersion, etc. In this manner synthetic rubber may be produced at the rate of about 30 to 40 pounds per hour from a single arm.

If the bath is agitated sufficiently to maintain the crumb suspended in the coagulant, a mixture of the crumb and coagulant may be drawn off at any desired level of the tank, with recirculation of the liquid after separation of the crumb. The separation may be effected by filtering, centrifuging, etc.

The process is applicable to the coagulation of dispersions of rubber-like and resinous materials generally with any coagulant. Modifications may be made in the apparatus as well as in the process without departing from the scope of the invention which is defined in the appended claims.

What I claim is:

1. The process of coagulating a dispersion which on coagulation produces a rubber-like product, which process comprises maintaining a bath of coagulant, feeding a plurality of streams of the dispersion to rapidly and continuously changing locations under the surface of the bath of the coagulant, whereby the streams of the dispersion are sheared into droplets which on coagulation product a crumb of rubber-like particles, allowing the resulting crumb to rise to the surface of the body of coagulant, breaking up at the surface any agglomerates formed therefrom, and then separating the resultant material from the surface of the body of coagulant.

2. The process of coagulating a dispersion which on coagulation produces a rubber-like product, which process comprises maintaining a bath of coagulant, feeding a plurality of streams of the dispersion to rapidly and continuously changing locations under the surface of the bath of the coagulant, whereby the streams of the dispersion are sheared into droplets which on coagulation produce a crumb of rubber-like particles.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
490,525	Werner	June 24, 1893
734,985	Spindler	July 28, 1903
1,320,323	Drucker et al.	Oct. 28, 1919
1,505,479	Maitland	Aug. 19, 1924
2,074,988	O'Brien et al.	Mar. 23, 1937
2,239,753	Martin	Apr. 29, 1941
2,366,460	Semon	Jan. 2, 1945
2,392,542	Matuszak	Jan. 8, 1946
2,393,208	Waterman et al.	Jan. 15, 1946
2,408,128	Squires et al.	Sept. 24, 1946
2,426,127	Thomas et al.	Aug. 19, 1947
2,431,478	Hill	Nov. 27, 1947
2,459,748	Johnson	Jan. 18, 1949

Certificate of Correction

Patent No. 2,495,147

JOHN N. STREET

January 17, 1950

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 39, for the word "product" read *produce*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of September, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.