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PATENT SPECIFICATION

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L192407



Inventor: CHERRAPPATHANATHU KURDUVILLA JOHN,
ARTHUR NEWSAM and BALACHANDRA CHAKKINGAL
SEKHAR

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COMPLETE SPECIFICATION

Improvements in or relating to the Coagulation of Natural Latex with Anionic Surfactants

We, THE BOARD OF THE RUBBER RESEARCH INSTITUTE OF MALAYA, a Body Corporate of Malaysia, of 3rd Mile Ampang Road, Kuala Lumpur, Malaya, 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:—

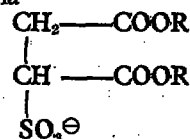
This invention is for improvements in or relating to the processing of natural rubber, and has the object of facilitating the production of rubber with a lower nitrogen content than is normally associated with it. Many attempts have been made to process natural rubber latex with reduced non-rubbers for specialised applications. The difficulty that is experienced in doing this is associated with the proteins that are normally present in the aqueous phase (serum) of *Hevea* latex. In the conventional method of coagulating *Hevea* latex, an organic acid is used to reduce pH to cause agglomeration of rubber particles. The use of acid not only agglomerates the rubber particles but also precipitates serum proteins which become occluded in the rubber coagulum. Alternative methods of coagulation involving heat, salt, etc., lead to the same result as far as proteins in the serum are concerned. There is therefore a great need to develop an economic and practical method of precipitating rubber particles from latex without the concomitant precipitation of serum protein.

Non-rubber constituents in latex can be advantageous or detrimental to the finished rubber. The serum proteins, however, do not confer to the finished product any advantageous characteristics of importance. On the other hand, rubber containing less protein has obvious superiority for certain applications. It is well known in the industry that cup coagulum, in which latex is allowed to undergo putrefactive coagulation in the collecting cups

without resort to any added acids, possesses generally a lower nitrogen content than conventional smoked sheet or crepe prepared by acid coagulation of latex. It is also known that for certain applications, particularly those where resilience and heat-build-up are important, consumers prefer the cup-lump material because of its lower protein content. Apart from such uses, in certain other applications a partially purified natural rubber is necessary and this is met by a process of centrifugation of latex; dilution of the concentrate and subsequent coagulation to remove the serum proteins, etc. Such methods are both cumbersome and costly.

We have discovered a simple and economic method of precipitating rubber from latex by an alternative path which does not involve the precipitation of serum proteins at the same time.

Our invention will allow the processing of *Hevea* latex by conventional methods to reach an end product containing a lower nitrogen content. The present invention provides a method of coagulating *Hevea* latex, which method comprises adding to the latex an anionic surfactant having an anion of the general formula



where R is a saturated alkyl group, in an amount to coagulate the latex. Compounds of this kind are commercially available in the form of their sodium salts. R is particularly a branched chain alkyl group of the formula $\text{C}_n\text{H}_{(2n+1)}$ where n is an integer from 4 to 9, the coagulating efficiency then increasing with chain length. The anionic surfactant should be present in an amount of at least 0.05% by weight on the dry rubber content. The coagulation time of undiluted *Hevea* field latex

can be made almost instantaneous by the addition of the requisite amount of anionic surfactant; in diluted field latex the coagulation time will be extended but in every instance
 5 coagulation will ensue at the requisite concentration of anionic surfactant, provided the dilution is not below 10% dry rubber content. Higher members of the series, up to $n = 18$, are also effective. In general, coagulating
 10 efficiency is affected by the solvent used. Although this type of surfactant, being anionic, would not normally be expected to cause the coagulation of rubber on its own, it has the inexplicable ability to cause agglomeration of
 15 *Hevea* latex rubber particles without the aid of any other additive.

In the normal procedure for concentrating *Hevea* latex, using centrifuges, the latex is divided into a fraction of high dry rubber
 20 content (60%) known to the trade as 'latex concentrate', and a fraction of low dry rubber content known to the trade as 'skim'. While the former is a premium product with many applications involving the use of rubber in
 25 liquid latex form, the rubber precipitated from the latter is a by-product and can only be sold at a discount. The disadvantages of skim rubbers are largely derived from their high protein content, sometimes in excess of 20%.
 30 The present invention, which allows the precipitation of rubber without precipitating the serum proteins, provides a practical method of converting skim latex into a rubber with satisfactory properties. In applying our inven-
 35 tion to this process attention must be paid to the high ammonia content of skim latex. While the specified anionic surfactants will not cause coagulation of latex containing excessive amounts of ammonia, this can be overcome by
 40 reducing the ammonia concentration of skim

by passage of air or steam. Additionally, skim may be mixed with unammoniated fresh field latex in proportions further to reduce the influence of ammonia prior to the addition of the anionic surfactant.

More specifically, the anionic detergents which we have discovered to be the more active of the group are sodium dioctyl sulphosuccinate and sodium dinonyl sulphosuccinate, available under such trade names as
 50 Aerosol OT, Aerosol GPG, Aponaid TH, Manoxol OT, and Manoxol N (MANOXOL is a Registered Trade Mark). The alkyl groups of these materials are believed to have branched chains. The effectiveness of these
 55 surfactants for the coagulation of *Hevea* latex is dependent on the alkyl group; for example the dinonyl ester is more effective than the dioctyl, while the di(isobutyl) is appreciably less effective than the dioctyl. It is to be
 60 expected that the properties of some esters having larger alkyl groups will, in an appropriate solvent, be at least as good as those of the dinonyl ester. Commercially available materials may be technically pure solids or
 65 solutions in water or other solvents.

Rubber precipitated with the type of anionic surfactants here specified has been shown to have a lower nitrogen content than rubber
 70 precipitated from the same batch of latex by the conventional acid coagulation procedure.

Table 1 shows the usual levels of nitrogen concentration found in rubbers prepared from latex by the conventional acid coagulation procedure (ribbed smoked sheet and air dried
 75 sheet) compared with the usual level resulting from biological (putrefactive) coagulation of latex (in cup-lump crepe). It will be seen that the biological

TABLE 1

Levels of nitrogen in representative samples of conventional smoked and air dried sheets and lower grade crepes

Type of rubber	Method of coagulation	Nitrogen content % by weight
Ribbed smoked sheet	Acid	0.38 — 0.55
Air dried sheet	Acid	0.35 — 0.50
Cup-lump crepe	Biological	0.23 — 0.42

coagulation process, which is carried out at a higher pH, gives a lower nitrogen content.

When the specified anionic surfactants are used for the coagulating procedure the pH
 85 remains well above six, approaching neutrality, indicating that the rubber is precipitated under pH conditions which will not precipitate the serum proteins.

The effects on serum proteins of an

organic acid conventionally used to coagulate rubber, and of the anionic surfactants which are more specifically the subject of our inven-
 90 tion, are illustrated by their action on *Hevea* latex serum obtained by ultracentrifugation of fresh field latex. Table 2 shows that, while
 95 acid addition to the serum causes precipitation of the proteins, the addition of the surfactants does not do so but leaves substantially all the

proteins in solution in the serum. It is thus clear that coagulation of *Hevea* latex by sodium dioctyl or sodium dinonyl sulphosuccinate will provide a rubber containing less protein by the amount remaining dissolved in the latex serum. This has been amply confirmed. We have estab-

lished that either in undiluted field latex form or in diluted field latex form, rubber coagulated by the specified anionic surfactants contains a lower nitrogen content than acid-coagulated rubber from the same batch of latex. We have further

TABLE 2

Effect of rubber coagulating agents on proteins in *Hevea* latex serum

Coagulating agent	Concentration % by weight on serum	pH of serum + coagulating agent	Effect on proteins
formic acid	0.155	5.0	Immediate precipitation
acetic acid	0.31	5.0	Immediate precipitation
Aerosol OT	0.1	6.92	No immediate precipitation and none or only
Anonaid TH	0.1	6.85	slight precipitation on
Manoxol OT	0.1	6.80	standing for 4 hours
Manoxol N	0.1	6.90	
None	—	6.80	Not precipitated in 4 hours.

confirmed that the serum left after coagulation of the latex or expressed from the coagulum has a higher nitrogen content when the rubber is coagulated by the anionic surfactants than when acid is used for coagulation.

The lowering of nitrogen content in rubber consequent on using the present invention has the technical merits that could be expected and are discussed in the introductory paragraphs. Technological properties determined on the resulting rubber using either a pure gum mix or a conventional carbon black filled formulation have shown that the rubber coagulated with the specified anionic surfactants (and thereby containing less nitrogen) is significantly superior in both resilience and heat-build-up properties.

The invention will be illustrated by the following examples. All percentages and proportions are by weight unless otherwise stated.

EXAMPLE 1

A litre of *Hevea* latex as obtained from the

tree was divided into two lots: the first 500 ml. lot was divided into sub-lots A, B and C. While A was retained as control, B and C were diluted to 20% and 10% dry rubber content respectively. A, B and C were then coagulated in the usual manner with formic acid at a pH of 5. The second 500 ml. lot was also divided into three sub-lots in a similar fashion, and two of them diluted to 20 or 10% dry rubber content. In this second lot coagulation was carried out by the addition of 0.25% (on dry rubber content) sodium dioctyl sulphosuccinate in the form of Aerosol OT. All coagula were granulated on a creping machine, in the usual fashion, dried at 140°F. overnight, and each sample was analysed for nitrogen. Table 3 shows the result obtained, indicating reductions in nitrogen content of the resulting rubber ranging from 14 to 23% when using the anionic surfactants to coagulate the rubber, as compared with acid coagulation.

TABLE 3

Nitrogen content of dry rubber produced by coagulating *Hevea* latex with formic acid or with Aerosol OT.

Sub-lot	Dry Rubber Content	Nitrogen Content % Coagulating system		% reduction in Nitrogen content
		Acid	Aerosol OT	
A	Field	0.37	0.30	19
B	20%	0.35	0.30	14
C	10%	0.35	0.27	23

EXAMPLE 2

The experiment described under Example 1 was repeated using the same bulk latex except in this instance sodium dioctyl sulphosuccinate at a strength of 0.1% on dry rubber content was used in its alternative form of

Anonaid TH. Results obtained with Anonaid TH, given in Table 4, are similar to those obtained with Aerosol OT, indicating reductions in nitrogen content ranging from 9 to 17%.

TABLE 4

Nitrogen content of dry rubber produced by coagulating *Hevea* latex with formic acid or with Anonaid TH

Sub-lot	Dry Rubber Content	Nitrogen Content % Coagulating system		% reduction in Nitrogen Content
		Acid	Anonaid TH	
A	Field	0.37	0.33	11
B	20%	0.35	0.32	9
C	10%	0.35	0.29	17

EXAMPLE 3

Fresh field latex was divided into two lots: the first was coagulated with 2% formic acid added to give a pH of 5.0, the second with 0.3% (on dry rubber content) sodium dioctyl sulphosuccinate as Aerosol GPG; after 4 hours the coagulum was crumbled and the crumbs soaked in water from which they were removed

at various intervals for drying and nitrogen estimation. Mean results of three experiments, recorded in Table 5, show that after coagulation with Aerosol GPG there is a small lowering of the nitrogen content on soaking the crumbs, the effect being obtained within the first hour.

TABLE 5

Nitrogen content (%) of dry rubber produced by coagulating *Hevea* latex with formic acid or with Aerosol GPG, after soaking the crumbs

Coagulating system	Soaking time (hr.)				
	0	1	2	3	4
Formic acid	0.42	0.42	0.43	0.41	0.41
Aerosol GPG	0.40	0.35	0.37	0.36	0.37

EXAMPLE 4

5 Factory bulk latex was divided into two lots: to the first lot formic acid was added to reduce the pH to 5.0, after which it was divided into a number of sub-lots and left to coagulate. The second lot was coagulated with 0.4% (on dry rubber content) of sodium dioctyl sulphosuccinate as Aerosol GPG and sub-lots similarly left to coagulate. One sub-

lot from each lot was taken at various intervals 10 after adding the coagulant, for granulation, drying and estimation of the nitrogen content of the dry rubber (Table 6). Initially the nitrogen level of the rubber coagulated with GPG was markedly lower than that coagulated 15 with acid but after 8 hours the difference was negligible.

TABLE 6

Nitrogen content of dry rubber produced by coagulating *Hevea* latex with formic acid or Aerosol GPG when processed after various periods.

Sub-lot	Coagulating system	Nitrogen content (%) when processed after (hr).				
		1	2	4	8	24
A	Formic acid	0.45	0.43	0.44	0.42	0.41
B	Aerosol GPG	0.38	0.36	0.39	0.41	0.41
% reduction in nitrogen		15.6	16.3	11.4	2.4	—

EXAMPLE 5

20 Latex collected from 9 common *Hevea* clones was divided into two lots: the first was coagulated with formic acid added to reduce the pH to 5.2, the second with 0.25% (on dry rubber content) sodium dioctyl sulphosuccinate as Aerosol OT. After 4 hours the serum was 25 removed, taken to dryness and the nitrogen content of the total solids estimated. The

coagulum was processed into dry rubber, the nitrogen content of which was estimated. Table 7 shows that coagulating latex with Aerosol OT in all cases gave a reduction of 30 nitrogen content compared to that of the acid coagulated rubber, the reduction varying with different clones. The reduction in nitrogen content of the dry rubber was associated with 35 the expected increase in the serum nitrogen.

TABLE 7

Nitrogen content of dry rubber and expressed serum of clonal *Hevea* latex when coagulated in the presence of formic acid or Aerosol OT.

Clone	Coagulating system	Nitrogen content (%)		% reduction in nitrogen from acid coagulation
		total serum solids	dry rubber	
PB 5/51	Formic acid	1.8	0.44	—
	Aerosol OT	2.1	0.37	15.9
PR 107	Formic acid	1.8	0.41	—
	Aerosol OT	2.2	0.33	19.5
Tjir 1	Formic acid	1.8	0.38	—
	Aerosol OT	2.1	0.34	10.5
RRIM 501	Formic acid	1.6	0.42	—
	Aerosol OT	2.0	0.38	9.5
RRIM 701	Formic acid	1.7	0.51	—
	Aerosol OT	1.9	0.45	11.8
RRIM 600	Formic acid	1.7	0.45	—
	Aerosol OT	2.0	0.37	17.8
RRIM 605	Formic acid	1.9	0.43	—
	Aerosol OT	2.1	0.38	11.6
RRIM 623	Formic acid	2.0	0.37	—
	Aerosol OT	2.3	0.33	10.8
RRIM 628	Formic acid	1.9	0.41	—
	Aerosol OT	2.0	0.38	7.3

EXAMPLE 6

Ordinary *Hevea* field latex was divided into three lots. The first lot was divided into three sub-lots, one coagulated with formic acid added to give a pH of 4.8, the second and third coagulated with 0.4% (on dry rubber content) sodium dioctyl sulphasuccinate, as Aerosol OT or Anonaid TH; all three coagula were then granulated and dried. Some of the second lot was ultracentrifuged to separate the latex serum layer from the 'cream' of rubber hydrocarbon, and the following experiment carried out: serum obtained from the ultra-

centrifugation was added to the remainder of the second lot to reduce the dry rubber content to 20%, and the serum/latex mixture was divided into two sub-lots, coagulated as before either with acid or with Aerosol OT, then granulated and dried. The third lot was treated in similar fashion to the second lot, except that Anonaid TH was used in place of Aerosol OT. The nitrogen contents of the resulting rubber samples, shown in Table 8, indicate reductions in nitrogen content that range from 5 to 33%.

TABLE 8

Nitrogen content of dry rubber produced by coagulating diluted and undiluted *Hevea* latex with acid, Aerosol OT or Anonaid TH

Sample	Dry Rubber Content	Nitrogen Content % Coagulating system			% reduction in nitrogen content
		Acid	Aerosol OT	Anonaid TH	
A	Field	0.42	0.35		17
		0.42		0.40	5
B	20%	0.67	0.45		33
		0.78		0.68	13

EXAMPLE 7

Two samples of skim latex initially of pH 9.6 and 9.9, partially de-ammoniated by passage of air while stirred, were separately mixed with two samples of fresh field latex in the proportions by volume 75 latex: 25 skim. The two mixtures, of pH 7.3 were divided into three lots. The first lot was coagulated with formic acid added to give a pH of 5.0; the second and third lots coagulated with sodium dioctyl sulphosuccinate, the second with 0.3% (on dry rubber content) as Aerosol OT and the third lot with 0.15% as Anonaid TH. The coagula were granulated and the resulting rubber samples analysed for nitrogen.

EXAMPLE 8

The full procedure of Example 7 was repeated with the same two samples of latex skim and the same two samples of fresh field latex, but this time mixed in equal proportions by volume, giving a pH of 8.6. The mixture was divided, coagulated and processed as before, and the resulting samples analysed for nitrogen.

The results obtained on the samples prepared as described in Examples 7 and 8 combined in Table 9, indicate reductions in nitrogen content of the resulting rubber ranging.

TABLE 9

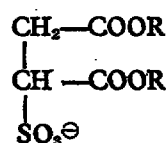
¹ Nitrogen content of dry rubber produced by coagulating mixtures of field latex and skim latex, with acid, Aerosol OT or Anonaid TH (mean of two experiments)

Latex mixture by volume		Nitrogen Content % Coagulating system			% reduction in nitrogen content
Field	Skim	Acid	Aerosol OT	Anonaid TH	
75	25	0.53	0.47		11
75	25	0.53		0.45	15
50	50	0.65	0.60		8
50	50	0.65		0.60	8

from 8 to 15%, when coagulation with the anionic surfactant is compared with acid coagulation.

WHAT WE CLAIM IS:—

1. A method of coagulating *Hevea* latex, which method comprises adding to the latex an anionic surfactant, having an anion of the general formula



where R is a saturated alkyl group, in an amount to coagulate the latex.

2. A method as claimed in claim 1, where-

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		Acid	Aerosol OT	Anonaid TH	
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		0.42			5
B	20%	0.67	0.45	0.68	33
		0.78			13

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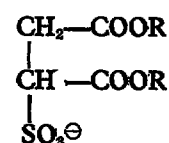
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75	25	0.53			15
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from 8 to 15%, when coagulation with the anionic surfactant is compared with acid coagulation.

WHAT WE CLAIM IS:—

1. A method of coagulating *Hevea* latex, which method comprises adding to the latex an anionic surfactant, having an anion of the general formula



where R is a saturated alkyl group, in an amount to coagulate the latex.

2. A method as claimed in claim 1, where-



in the *Hevea* latex is used in the concentration in which it is obtained from the tree.

3. A method as claimed in claim 1, wherein the *Hevea* latex is used in a diluted form containing at least 10% dry rubber solids.

4. A method as claimed in claim 1, wherein the latex includes a skim fraction of low dry rubber content formed as a by-product in the production of a latex concentrate of high dry rubber content.

5. A method as claimed in any one of claims 1 to 4, wherein R is a branched-chain alkyl group of the formula $C_nH_{(2n+1)}$, where n is an integer of from 4 to 9.

6. A method as claimed in any one of claims 1 to 5, wherein the anionic surfactant is used in the form of its sodium salt.

7. A method as claimed in any one of claims 1 to 6, wherein the anionic surfactant is sodium dioctyl sulphosuccinate.

8. A method as claimed in any one of claims 1 to 6, wherein the anionic surfactant is sodium dinonyl sulphosuccinate.

9. A method as claimed in any one of claims 1 to 8, wherein the anionic surfactant is used in an amount of at least 0.05% by weight on the dry rubber content of the latex.

10. A method as claimed in claim 1 and substantially as hereinbefore described in any one of Examples 1 to 8.

11. Natural rubber when coagulated from *Hevea* latex by the method claimed in any one of claims 1 to 10.

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
Agents for the Applicants.
5 Quality Court, Chancery Lane,
London, W.C.2.

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