Patented May 15, 1928. 1,669,491

UNITED STATES PATENT OFFICE.

WALLACE SAVAGE, OF ELIZABETH, NEW JERSEY, ASSIGNOR TO SAVAGE-RUBBER CORPORATION, OF NEWARK, NEW JERSEY, A CORPORATION OF NEW JERSEY.

TREATMENT OF FATTY STILL RESIDUES.

No Drawing. Application filed June 12, 1923. Serial No. 644,039.

This invention relates to the treatment of fatty still residues and compounds containing such residues and embraces the processes of treatment and the various features thereof and the products obtained thereby.

When fatty acid still bottoms, tars and pitches are cured under proper conditions by means of vulcanizing reagents of the type applied in the curing of rubber, a new, congealed, highly resilient pitch product is obtained. These resilient pitches have much in common with vulcanized rubber, are not weak and crumbly like oil rubber substitutes, and give strong compounds with special and distinct characteristics.

The temperature range of the resilient state varies, plastic flow being ordinarily attained at from 100 to 180° C. and vitreous fractures occurring at temperatures as low as −15° C, according to the character and treatment of the fatty material vulcanized. Resilient pitch products of wide range in properties can be obtained from any source of fatty still residues; by blending and compounding the crude still bottoms, tars and pitches with one another or with other compounding ingredients; by dehydrogenation of the hydrocarbon with reagents such as air, steam, sulphur dioxide, sulphur, or dehydrogenation catalysts such as finely divided metals, iron grindings, for example; by desaturation by means of pyrolysis and chemical decomposition of the fatty carboxyl group; by neutralization of all or a portion of the free acid component of the fatty tar to be cured; by the use of vulcanization accelerators to obtain optimum vulcanization conditions and cures; and by means in conjunction with these and various other features to be more fully described hereinafter.

Among the objects of this invention are to provide processes and process steps for the treatment of fatty still residues having unstable and plastic properties to produce improved products having satisfactory and desirable fixed and resilient characteristics, and to provide improved resilient pitch products.

The fatty still residues which may be used in the production of resilient pitch products according to the present invention, include the residue oils, fatty acids, tars and pitches obtained by the distillation of animal and vegetable oils and fats, and in particular of fatty acids rendered volatile for distillation by saponification of any fatty glycerides. Residues, tars and pitches of this character are obtained in connection with the manufacture of distilled soap stocks, distilled stearine and hydroxy stearine, candle fats and the like, from such fatty sources as corn oil, cotton seed oil, fish oils, tankage and garbage greases, and the like. As it is not feasible to complete the decomposition of the fatty material constituting combined glycerine base with fatty organic acids, by any practical saponification process, due to the equlibrium set up by the reverse process through the recombining effect of the free organic base and acids, the fatty acid stock charged into the still usually contains from 10% to 20% of combined glyceride fatty matter. This oil or fat being non-volatile remains as a constituent in the still bottom residues and after completion of the distillation process will be discharged as a tar or, if sufficiently heated, as a pitch of varying consistency. The glycerine base may be dehydrated to a considerable extent, yielding the mono-organic base, acrolein. With equal heating conditions, the still residues from oil sources are softer than those from the fat sources, with the tallow like raw stocks forming the hardest and linseed stocks about the softest, due to the fluxing tendency of the content of glyceride or acroleide fat esters in the residue. In general, the more unsaturated the fatty acid, the more fluid the oil or fat and the softer the still bottom residue obtained with it will be.

The still bottom residues obtained as an initial by-product in the refining by distillation of fatty acids derived from vegetable and animal oils are thick, sticky, brownish-black, tar like oils or pitches having a melting point in the neighborhood of from 15° to 50° C. They usually retain from 15% to 30% of free fatty acids, which cannot be distilled off without serious decomposition of the fatty acid carboxyl group, producing a discolored distillate of decreasing fatty acid and saponification value. These residues may be superheated to obtain a low grade pyro-fatty acid distillate and destructively distilled pitch. If this fraction of fatty acids is taken off, it may be segregated as a tailing and reworked by mixing with the next charge for distillation, many volatile hydrocarbon impurities thus being introduced into the stock, which is undesirable in the manufacture of high grade soap stocks

but good practice in the case of burning stocks such as for candles, when acid value is immaterial. An oil of fatty content of from 15 to 30% has previously been alluded to. The remaining portion is made up of polymerized fatty acids, fatty acid anhydrides and asphalt like inert hydrocarbon products resulting from a certain unavoidable amount of thermal decomposition. If pyrolytic distillation is carried very far, the latter portion begins to predominate, giving a pitch verging into asphalt in all of its physical characteristics. Pitch of this type has been known as candle tar or candle pitch. This material may be utilized in paint or roofing or similar uses where the stearines are preferable because of their more saturated chemical nature, greater stability to weathering and lesser tendency to oxidize than the less saturated oil pitches. However, as all vegetable and animal fats and oils are mixtures of a few predominating fatty acid esters differing but slightly in molecular weight and only materially in the number of double bonds, which can be altered at will by chemical and physical treatment, the nature of the source of the oil or fat or fatty material is not of fundamental importance.

Briefly, the process steps of the present invention include preheating, blending and compounding, curing with vulcanization agents or polymerization agents such as sulphur or its equivalent in conjunction with organic and inorganic bases, capable of changing the oily free fatty acid content from an undesirable solvent phase to a colloidal filler phase, and thereby accelerating and aiding the curing process, cooling the product, and casting, molding and mechanically treating the cooled product. The various features of this invention may be used in conjunction with each other or applied separately.

Prior to vulcanization, the fatty residues tars or pitches to be vulcanized may be subjected to treatment to obtain material of standard and uniform consistency for the production of the desired product. Normally, the harder pitches yield a harder product than the softer pitches and tars. The softer tars and pitches may be hardened to any required extent by destructive distillation with or without steam or air blowing, by saponification with bases such as magnesia or lime or by incorporating hard bitumens such as hard fatty pitch, asphalt, grahamite gilsonite, mineral rubber, or the like therein. All intermediate stages between extremely soft and very hard properties can be obtained in the vulcanized residue. Harder pitches may also be softened by blending therewith fluxes such as solvent aromatic, terpene, or paraffin oils, fatty acids or their glycerides prior to vulcanization. Where flexibility at low temperature is required, the addition of oils or oily material is advantageous. The amount of oil should be restricted below the point at which the product becomes crumbly or plastic. As high as 40% of linseed oil gives a strong product and as low an amount as 5% has a beneficial effect by increasing the volume of the vulcanized oil enveloping phase of the final product.

When vulcanization to a resilient cure is sought by the action of sulphur alone, the product obtained is of poor quality. Such products are resilient over but a very small temperature range, between the vitreous and plastic state, due to the severe heat necessary to reduce or decompose the solvent oil phase of the free thio fatty acids. If the usual solvent definition of vulcanized cure, as accepted in the rubber art, is applied, the completely vulcanized state or cure is not attained by the use of sulphur alone, due to the fact that all such products are soluble in solvents, such as carbon disulphide, benzol, naphtha, and the like. Where reagents that react with the carboxyl group are used, the fatty acid is eliminated as a source of trouble and contributes desirable properties when combined into a colloidal dispersed mineral soap or into some similar organic compound of sufficiently high melting point. Such products are not soluble in ordinary solvents and meet the above test for cure in the same manner as rubber does. This weakening effect, as exhibited by the solution in solvents, which is caused by the free fatty acid phase, may advantageously be applied by partial neutralization to give a product of satisfactory cure and can be readily milled, mixed with and thoroughly incorporated into such mediums as rubber or rubber compounds, in which it may be neutralized and cured upon vulcanization of the compound. In place of sulphur and a base, curing agents having equivalent effects may be employed. Sulphur chloride and phosphorous chloride modify the fatty acids satisfactorily and bring about an individual type of cure which is characteristic of the curing reagent. Bromine, iodine, chlorine, free or compounded with sulphur, selenium, antimony, arsenic, zinc or phosphorous, sulphur dioxide, the oxides of nitrogen, and their equivalents and chemically active compounds of them also yield characteristic cures.

The amount of sulphur required to bring about resiliency and cure amounts to at least 7% at temperatures between about 150° C. and 200° C. The rate of vulcanization is extremely slow below about 135° C. At 167° C. the reaction proceeds very favorably and at 185° C. excessive foaming begins so as to require violent agitation to confine the mass in a heating container of reasonable size. Five or six percent of sulphur does not develop a completely resilient state no matter what time and heat are used, but by adding

sulphur enough to bring the amount up to about 7% a cure can quickly be obtained. About 8% of sulphur is the best amount for general use, though where excessive free crystalline sulphur is not objectionable as much as several times this amount can be used. The sulphur should be finely divided or molten when added to the fatty tar or pitch to be treated. Molecular equivalents of other vulcanization reagents at temperatures giving equivalent vapor concentration and chemical reactivity will yield corresponding cures.

The process of vulcanization may be effected by mixing curing agents with the compound comprising the fatty residues, tars or pitches, and subjecting the mass to suitable temperatures in any convenient apparatus. The vulcanization may be completed in a single step or carried out in stages. For example, 95 parts of fatty acid still residue may be heated to 175° C. in a suitable container provided with a mixing and agitating device, and 5 parts of linseed oil, 5 of basic magnesium carbonate, 2 of aniline oil and 8 of sulphur flour then incorporated into the molten mass. If the temperature is maintained about one hour the product will gradually thicken, eventually congealing to a liver like consistency, when the hot cure is attained. Or 80 parts of fatty tar may be melted down and 20 parts of a fatty oil such as linseed oil, 10 parts of sulphur, 5 of basic magnesium carbonate, 2 of lead oxide, 2 of thiocarbanilide and 3 of zinc oxide then incorporated into the mass at a vulcanization temperature. Or, as a further example, 8 parts of sulphur, 5 of basic magnesium carbonate or 2 of magnesium oxide and 3 of magnesium carbonate and 2 of aniline may be incorporated into 100 parts of fatty pitch at a temperature between about 150° and 180° C.

Usually it is best to allow the final cure to take place in the molds, into which the charge is cast in a semi-cured state, the heat in the mass being sufficient to maintain prolonged and gradually diminishing vulcanizing temperatures which do not give an over or dead cure as may happen where the product is kept under a high heat head such as would be applied to the vulcanizing container. The final cure is best effected by cooling the reaction product very slowly. Under-cured resilient pitches mill better with rubber than do either the raw still residues or the completely cured product, the latter being more difficult to disperse in the gum and the raw pitch causing sticking on the mill rolls. Very slight under cures are often desirable as the product in aging cures to a small extent and improves in quality rather than taking on an over cure. Too much under cure is fatal, due to atmospheric oxidation which induces a hard, brittle, non-resilient character in the material which will eventually become vitreous and brittle, similarly to the raw fatty acid residues upon weathering.

Spread films may be advantageously cured by exposure to sulphur dioxide. For example, the fumes from burning sulphur carrying some sublimed sulphur, in amounts of about 20 parts of sulphur dioxide and 3 of sulphur, may be passed through a chamber where fabrics coated with about 100 parts of fatty tar are exposed. A considerable amount of hydrogen sulphite is developed which reacts with the sulphur dioxide. A cure is obtained in about 10 minutes. Similarly, gases of equivalent compositions may be blown through molten pitch. A halogen proof packing material may be made, for example, by vulcanizing 100 parts of fatty pitch with about 20 parts of bromine iodide and 5 parts of zinc oxide.

The vulcanization reaction is exothermic and it is frequently advantageous to control the final cure by withholding a portion of the sulphur and adding this portion after the major reaction has been effected and after the reaction mass has slightly cooled. A semi-finished product that can be stored and transported at any temperature can be obtained by combining the pitch with only a part, say from ½ to ⅔ of the sulphur required to fully vulcanize it. This material may then be finished by adding the remainder of the sulphur and subjecting the semi-vulcanized material with the added sulphur to a temperature of about 150° C. for a few minutes. Or the pitch may be combined with a part of the sulphur at high temperature, the semi-vulcanized product then cooled below about 135° C. and the remainder of the sulphur required to effect the vulcanization then incorporated in the batch. Such products can be stored indefinitely and can be finished at any time by merely heating to the vulcanization temperature. A semi-finished product may likewise be prepared by incorporating the entire amount of sulphur necessary to effect vulcanization into the fatty still residue or compound thereof at a temperature below the point at which the vulcanization reaction proceeds, that is, below about 135° C. Such products may then be finished at any time by heating to a temperature above 150° C. If part of the sulphur is withheld from the charge, the mass can be maintained for an indefinite period in the fused state or can be cooled, fused again, stored, transported and compounded with any compatible material and can be finally cured by treating with a further amount of sulphur. Insufficient heating of the complete compound is frequently convenient as well as withholding the full amount of the accelerating bases or of the sulphur.

Where the fatty pitch contains too large

an amount of staurated fats such as stearic or palmitic acids of the acetic series to yield a product of the required elasticity and resiliency, it may either be compounded with sufficient of those acids of the oleic, linoleic, linolenic or risinoleic series to dilute the waxy phase or may be desaturated or dehydrogenated by heating with 4 to 5% of sulphur at a relatively high temperature, usually above 200° C. and preferably not over 300° C. The reaction proceeds violently and it is best to add the sulphur in small intermittent portions. For example, if 100 parts of stearine candle tar are heated with 4 parts of sulphur at a temperature of 250° C. the pitch will be dehydrogenated with evolution of quantities of hydrogen sulphide, forming a saturated thio fatty acid. The amount of sulphur required to finish a cure may be added after the product has cooled to about 175° C., and the other vulcanizing agents have been incorporated. Hydroxystearines can be desaturated by heat alone.

The fatty pitches due to their origin are always highly acid and any free fatty acid, even when saturated with sulphur, left in the resilient pitch product limits the resilient cure and induces plasticity. The more acid products are meltable and self-healing, whereas products in which the free thio faty acids have been substantially neutralized are more rigid, are not self healing, and are not meltable by the application of dry heat alone. With more than 25% free thio fatty acids present, no resilient state can be obtained. Resiliency appears very slowly with 17% free acids present but fair cures begin when less than 10% are present. Most excellent products are obtained with the lowest amounts of free fatty acids, that is, in the neighborhood of 3%. These free fatty acids may be neutralized partially or entirely with active bases such as lime, magnesia, zinc oxide, magnesium carbonate, aniline oil, and the like, forming a colloidal soap or amine phase dispersed through the product. Such dispersed soaps are particularly advantageous for certain purposes, such as in rubber compounds.

In order to obtain a substantially optimum cure, it is always necessary to use some good vulcanization accelerator. These include all active bases heretofore mentioned as neutralizing agents as well as organic accelerators such as diphenylguanidine and triphenylguanidine and aniline products such as ethylidene aniline, formaldehyde aniline, triocarbanilide, toluidene, and the like, also other types of bases such as hexamethylene tetramine, lead oleate, etc., such as are used in curing rubber containing free resinous acids. Amines are usually suitable. All alkaline substances in general will effect the necessary acceleration, although the caustic alkalies such as sodium and potassium hydroxide are not desirable because their fatty soaps are soluble. Magnesia is a good accelerator but the magnesium oxide gives an excessively rapid cure. Basic magnesium carbonate obtained by partial recarbonation of magnesium oxide is, in general, preferable. These alkaline bases and accelerators apparently serve a dual function, serving to fix the free fatty acids in a desirable phase and to accelerate the curing reaction in general.

The hot vulcanized product, while fused or plastic, has a tendency to adhere to molding surfaces and the best method of surmounting this obstacle is to mold the product on wet surfaces. The water film instantly cools the outer skin of the material and prevents it from fusing onto the molding material. Wet fabrics, paper, or cloth on which soapstone has been powdered, give satisfaction. Amalgamated copper may be used where the presence of water is undesirable.

Fillers such as aluminum flake, asbestine, aluminum silicate, barium carbonate, barytes, blanc fixe, chalk, china clay, cotton flock, cotton linters, fossil flour, graphite, infusorial earth, mica, pumice, rotten stone, silica, soapstone, talc, terra blanche, tripoli flour, whiting, wood pulp, mineral rubber, cumar resin, pine tar, Burgundy pitch, rosin, black substitutes, paraffin wax, carbon black, iron oxide, lampblack, lithopone, titanox, zinc oxide, and the like, and their equivalents, may be compounded with the resilient pitch or resilient pitch rubber products. These fillers may be worked into the product on a rubber or kneading mill or may be stirred into the liquid fatty tar prior to its vulcanization. Free sulphur in excess of that required to effect vulcanization also acts as a filler.

Resilient pitch products are particularly adapted for use in compounding with rubber. Resilient pitches, particularly when they contain a colloidal soap phase resulting from neutralization of free fatty acids therein, act as lubricants in the rubber compound, decreasing the amount of internal heat, and also act to water-proof the rubber compound. The following examples are illustrations of suitable rubber compounds:

Fatty still residues	95	200	190
Linseed oil	5		10
Rubber	800	200	200
Sulphur	50	26	26
Magnesia	4	5	5
Litharge	6		
Aniline	16	4	4
Thiocarbanilide	2	4	4
Magnesium carbonate	6	6	6
Zinc oxide	300	50	50
Carbonblack	100		
Mineral rubber	25		

The components can be all compounded in one stage, but it is much more expedient to

make such a resilient pitch product such as the first specifically described herein, substantially cure it, and then mill it into the rubber with the usual rubber compounding ingredients. The pitch may be vulcanized prior to introduction into the rubber, or the rubber and pitch may be vulcanized together. Likewise, the pitch may be partially vulcanized and the vulcanization completed in conjunction with the vulcanization of the rubber compound. Resilient pitch acts as a softening agent on the mill, causing the fillers to disperse better and with less friction, heat and depolymerization of the rubber stock. Colloidal fatty acid soap in the resilient pitch aids in obtaining a good strong cure and is an ameliorating agent of considerable value. Automobile tires containing rubber compounded with resilient pitch have proven satisfactory over extensive road tests.

Resilient pitch products are resilient compositions of very general application. They are water proof. They have given satisfactory service in jointing concrete over a test period of twenty months. They are suitable for use as a packing material, for liquid, vapor or gas-tight joint seals, such as are required for pipe gaskets, concrete roofing, tanks, dams, conduits, subways, roads and building foundations. They are resistant to the attack of strong acids such as muriatic acid. They are moisture repellant and have good dielectric properties. They can be shaped by molding, hot pressing or cutting into very inexpensive resilient pitch articles of fair quality or into economically produced resilient pitch rubber articles of highest quality.

In my co-pending application, filed Jan. 17, 1922, Serial No. 529,963, I have described and claimed processes and products related to the subject matter of this application.

The term fatty still residues, as used herein, is intended to include all the various generic terms which have been or may be used to designate these fatty acid still bottoms, tars and pitches, including candle tar, kerzenterr (German), gondron (French), candle pitch, fat pitch, stearine pitch, palm oil pitch, bone-fat pitch, cotton-seed oil pitch, cotton pitch, cotton-stearine pitch, cotton seed foots pitch, corn oil pitch, corn oil foots pitch, packing house pitch, garbage pitch, sewage pitch, fuller's grease pitch, wool pitch, wool grease pitch, wool fat pitch, cholesterol pitch, beta pitch, pitchene, vacuum pitch, fatty acid pitch, carboxylated petroleum pitch, synthetic fatty acid pitch, and the like, including tars and pitches from all vegetable, animal and mineral sources of fatty acids, their compounds and allied products, without regard to their degree of distillation, physical or chemical characteristics, source or process of manufacture.

While the preceding description has been specific to many details, it will be understood that examples have been given as illustrations of the broad principles of the invention set forth and are not to be considered as limiting the scope of the invention as many alterations and variations thereof will appear to those skilled in the art, all without departure from the spirit of my invention or the scope of the subjoined claims.

I claim:

1. The process which comprises treating fatty still residues and compositions containing the same with vulcanizing agents including an active alkaline component.

2. The process which comprises treating fatty still residues and compositions containing the same with sulphur and an organic accelerating base.

3. The process which comprises treating fatty still residues and compositions containing the same, with sulphur, an active base and an organic accelerating base.

4. The process which comprises treating fatty still residues and compositions containing the same at temperatures between about 135° C. and 205° C. with sulfur and an organic accelerating base.

5. The process which comprises reducing the free fatty acid content of fatty still residues and compositions containing the same to less than 17% and treating the same with vulcanizing agents.

6. The process which comprises reducing the free fatty acid content of fatty still residues and compositions containing the same to less than 10% and treating the same with vulcanizing agents.

7. The process which comprises subjecting fatty still residues and compositions containing the same to the action of vulcanizing agents including sulphur at gradually decreasing temperatures whereby to effect the final cure at a slow rate.

8. As a product, vulcanized resilient pitch comprising fatty still residues, a curing agent, an active base, and an organic vulcanization accelerator.

In testimony whereof I affix my signature.

WALLACE SAVAGE.