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LINOLEUM AND LINOLEUM CEMENT.

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To all whom it may concern:

Be it known that I, ALFRED BREWERTON CRAVEN, subject of the King of Great Britain, residing at Selby, in the county of York and Kingdom of England, have invented certain new and useful Improvements in and Relating to Linoleum and Linoleum Cement, of which the following is a specification.

This invention relates to improvements in the manufacture of linoleum and linoleum cement.

The present methods in use, oxidize linseed oil by the scrim process of slow oxidation and the Walton & Brinns-Bedford processes of quicker oxidation in the oxidizers known by those names and the temperature used is about 60° C. In the latter processes the product of oxidation is run out of the oxidizers whilst still fluid at 60° C., but sets on cooling to a gelatinous spongy mass. Both these oxidized oils are cemented by melting with rosin and kauri gum to impart tackiness and adhesiveness and the result is linoleum cement. Other methods of producing linoleum cement from linseed oil have been used or are in use to a smaller extent and consist of heating the linseed oil to very high temperature approaching 300° C. with a slow current of air bubbling through until the oil is polymerized and oxidized to a resilient tacky and adhesive mass without cementing. Alternatively the linseed oil is partially oxidized in an oxidizer of the types described at a temperature of 120–160° C. until the product is just set to a gelatinous mass when cold but which will still become again semi-fluid on heating to higher temperatures and this product is then made into a linoleum cement by a finishing operation of polymerizing at a temperature of about 200° C., with addition of gum and rosin. These processes of oxidation are particularly suitable for linseed oil on account of its ready oxidation at low temperatures to a gelatinous mass. The processes have also been applied to a limited extent to tung oil and soya oil both of which are readily oxidized.

I have discovered that this process of oxidation can be extended and adapted to produce linoleum cement from the less readily oxidizable oils usually known as partly drying oils or their fatty acids or mixtures of these fatty acids and glycerides as well as to the fatty acids of linseed oil and other readily drying oils. In fact any oil which contains liquid unsaturated higher fatty acids more unsaturated than oleic acid (either as free fatty acid or as glycerid, or as mixtures thereof) may be used in this process.

The liquid and semi-solid by-products obtained from all these oils when they are refined for edible and other purposes may also be employed including the by-products from drying oils. The refining operations which yield the by-products I use, are those generally in use, and consist of for example, (*a*) treatment of crude oil with a small quantity of strong soda lye, sufficient to combine with the free fatty acids present, and to leave a slight excess of caustic soda, agitating well, and warming gently, then allowing to stand, when the soap formed settles to the bottom, carrying down with it what is called "foots," containing colouring matter, mucilage and some of the oil itself. The clear refined oil is run off, and leaves the foots as by-product, which I acidify with mineral acid to convert the soap into fatty acids, and I then wash to remove mineral acid. (*b*) Refining by acid treatment, which consists of heating and agitating the crude oil with a small amount of slightly diluted sulphuric acid and allowing to stand. When the clear oil is run off, the sediment consisting of mucilage and oil, is a suitable by-product after being washed free from mineral acid. (*c*) Similar sediments resulting from other processes of refining such as treatment with dichromate of potash and mineral acid, and any sediment formed when a partly refined oil, or boiled oil, is allowed to stand in tank, are all suitable for my process. (*d*) The oily matter absorbed by fullers' earth which has been used in refining is also suitable, after the same has been extracted from the fullers' earth by a volatile solvent or by other means.

If necessary a preliminary treatment may be given, with the object of making a more suitable linoleum cement, bleaching by any known means, or distillation (see my British Patent 121,777) to remove part or all of the non-drying portion of the fatty acids, glycerides or mixtures, and to leave a partly polymerized residue, possessing greater dry-

ing properties. Any one, two, or all these treatments may be given to the same material.

The products of oxidation of the above materials differ from the oxidation product of linseed oil in that they are usually sufficiently tacky and adhesive for use as linoleum cement as run out from the oxidizer. Rosin and gum resins may however be added to increase the tackiness and adhesiveness if desired. The products of oxidation of the above materials are firmer or less firm, than cemented oxidized linseed oil depending upon the drying properties of the raw materials used, and also depending upon the extent of the removal of non-drying matter in the preliminary treatments, and this firmness may be adjusted to that required to give a most satisfactory linoleum by blending the products from the drying oils and the partly drying oils, either before oxidation, during oxidation, or after running off from the oxidizer.

The firmness of the oxidized products is due to the presence of the more highly unsaturated acids or their glycerides such as those of clupanodonic acid, linolenic acid and linolic acid. The softness of the oxidized products is due to the oleic acid or other less highly unsaturated acid or its glycerides.

I also find that by adding aluminium hydrate, during or before oxidation I can increase the tendency to yield a product resembling that obtained when linseed oil is oxidized in the usual way.

Previous attempts to make a satisfactory linoleum cement from partly drying oils have not been successful because all such oils contain a large proportion of the glyceride of oleic acid, and also have present glycerides of saturated fatty acids such as palmitic acid, stearic acid and myristic acid, which are relatively stable solid fats at ordinary temperatures. The effect of the presence of the large proportion of the glyceride of oleic acid is to render the oxidation product too soft and greasy, and a linoleum made from such an oil does not mature in the stoving, but remains soft and is not durable. The effect of the solid saturated glycerides is to reduce adhesiveness in the oxidation product and to cause linoleum to crack on bending. The treatments of filtration and distillation before oxidation to which I subject the various materials I make into linoleum cement are designed to reduce the proportion of the above mentioned glycerides. If however I am working with fatty acids or mixtures of fatty acids and glycerides the same treatments of filtration and distillation remove the fatty acids aforesaid which are quite as detrimental as their glycerides for my purpose. The result is a higher proportion in the oil products after treatment, of the glycerides or fatty acids which give the firm solid products by oxidation. By these means I am therefore able to obtain from partly drying oils linoleum cement equal to that from linseed oil.

In the case of linseed oil fatty acids oxidation may be proceeded with or without filtration or distillation, but if filtered and the clear acids only are oxidized, a better cement results, and further if the clear acids are distilled in a current of superheated steam, which is the method of distillation I prefer for all cases, until about 15% of the weight is removed, the residual fatty acids yield a still further improved cement after oxidation having great firmness and producing a linoleum which ages well and allows of bending without any great tendency to crack.

The alumina hydrate treatment imparts firmness and solidity to the oxidation product even when oleic acid or its glyceride is present in large proportion, and is an alternative method of obtaining the required firmness in the cement. The action of the aluminium hydrate is to combine with part of the oxidized fatty acids forming a non-greasy solid product.

It is preferred that the process proceed under conditions of higher temperature than is usual in the case of linseed oil, and a larger proportion of driers is used. The oxidation process is effected by gaseous oxygen and may be carried on in an oxidizer, capable of producing intimate contact between the material to be oxidized and the air or oxygen which is passed through the oxidizer. I use the term oxygen to include not only gaseous oxygen, but also ozone which of course can be used to shorten the time of oxidation but as it is more costly and as its action is less easy to control I prefer to use ordinary oxygen.

The temperature is maintained at about 80° C. until thickening is well advanced and then the temperature is raised to 100–110° C. and continued thereat to the end. Preferably not less than 1% of rosinate or linoleate, or an equivalent amount of the hydrate or other suitable compound of lead, manganese or cobalt is added at the beginning. After about 18 to 25 hours i. e. longer than is usual when linseed oil is oxidized, there results a mass which is non-fluid, resilient, tacky and adhesive at the temperature of working and this can be used direct as linoleum cement. This differs from the usual treatment of linseed oil which is run out as a fluid which sets to a gelatinous mass on cooling. An addition of resinous bodies may be made. If aluminium hydrate is added before or during oxidation, to an amount less than sufficient to combine with all the free fatty acids present, a shorter time is required to produce a

resilent mass, but the mass is then less adhesive and less tacky. In order to render this product sufficiently tacky and adhesive, additions of resinous bodies must be made preferably near the end of the operation, but subsequent to the addition of aluminium hydrate.

Alternatively the oxidation may be stopped before a non-fluid product is obtained, and the aluminium hydrate added to the charge, heat and agitation being maintained until a non-fluid resilient product is obtained.

Any of the fatty acids or mixtures aforesaid may be used separately or blended with each other.

It will be noted that the linoleum cements I make are distinct from the varnish or paint-like products which are used to spread on fabric, and after drying form "American cloth", and also distinct from the similar viscous paints used to decorate the surface of linoleum and oil-cloth. My linoleum cements are for use in the manufacture of linoleum in the usual way by incorporating with cork or wood fibre and pigments and pressing or rolling under pressure upon a fabric backing.

Example 1.

Ten hundredweights of fatty acids from linseed oil are charged into a Brinns-Bedford, or a Walton oxidizer, 1% (on the weight of the fatty acids) of rosinate of cobalt added, and the charge heated up. Air is blown through and the agitator set in motion. The temperature is maintained at 80° C. until it is only just fluid at this temperature when the temperature is raised to 100–110° C. until the product in the oxidizer, at this temperature, becomes non-fluid. The charge is then emptied and is ready for use as linoleum cement. The time required is about 14 hours. Mixtures of fatty acids and fatty oils (entirely or partially more unsaturated than oleic acid or olein) can be used in an analogous manner. Aluminum hydrate can be added before or during the oxidation step, this step being of especial utility when oils containing large quantities of oleic acid are employed. The fatty acids treated may be crude, or partially purified by the distillation and filtration method above referred to.

Example 2.

The foots from a partly drying oil, for example cottonseed oil, (obtained in the refining operation described above under (*a*)) are filtered cold and ten hundredweights of the clear oil is charged into an oxidizer of one of the types mentioned in Example 1. 1% of rosinate of cobalt is added and the charge heated, and air blown through, with the agitator running. The temperature is maintained at 80° C. until the oxidation is well advanced but before a non-fluid state has been reached an addition of 3% aluminium hydrate in paste form is made. The running is continued at 100–110° C. and as soon as the aluminium hydrate has dissolved the charge becomes nonfluid. Now, two hundredweights of rosin and one hundredweight of kauri gum are added, and the temperature maintained as before with the agitator running slowly. As soon as the charge has become homogeneous it is emptied from the oxidizer as a non-fluid mass suitable for use as linoleum cement. The time required is about 24 hours.

Example 3.

As an illustration of the blending to give the required firmness in the cement, I take linseed oil acids and filter clear, then distil off about 15% by weight. The resulting fatty acids I then blend with one third of their weight of clear cod oil and oxidize the mixture with air or oxygen as described, when a product of satisfactory firmness results in about 14 hours.

Example 4.

I take cod oil fatty acids or cod oil or mixtures of the two and filter to remove solid fats or fatty acids. The clear oily matter obtained is now subjected to distillation with superheated steam to remove the solid fatty bodies still in solution and also to remove the non drying bodies. When one third of the charge has distilled over the still is emptied and the residue is transferred to an oxidizer and blended if desired with an equal quantity of the aforementioned by-products from refining cotton seed oil and the whole oxidized at 110° C. if the cotton seed by-product has been added or at 80° C. if the cod oil distillation residue alone is being oxidized. When the oxidation has proceeded so far as to produce a very viscous product 1% aluminum hydrate is added to pasty material and the oxidation continued. As soon as the charge has become gelatinous an addition of 15% rosin and 15% kauri gum is made and the running continued until the whole becomes non-fluid, resilient, tacky and adhesive when it is run out and is ready for use as linoleum cement.

I declare that what I claim is:—

1. The improvement in the manufacture of linoleum cement from substances containing radicals of the fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, but excluding drying oils which consists in subjecting said substances to an oxidation process capable of yielding a resilient adhesive and tacky product.

2. The process for the manufacture of linoleum cement from substances containing radicals of the fatty acids derived from

oils containing fatty acids more unsaturated than oleic acid, but excluding linseed oil, tung oil and soya oil as glycerides which consists in subjecting said substances to an oxidation process by a gas containing free oxygen capable of yielding a resilient adhesive and tacky product.

3. The process for the manufacture of linoleum cement from substances containing radicals of the fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, but excluding linseed oil, tung oil and soya oil as glycerides which consists in subjecting said substances to an oxidation process and adding aluminum hydrate at any stage of the process to yield a resilient adhesive and tacky product.

4. The process for the manufacture of linoleum cement from substances containing radicals of the fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, but excluding linseed oil, tung oil and soya oil as glycerides which consists in subjecting said substances to an oxidation process capable of yielding a resilient adhesive and tacky product and incorporating with rosin and suitable gums.

5. The process for the manufacture of linoleum cement from substances containing radicals of the fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, but excluding linseed oil, tung oil and soya oil as glycerides which consists in adjusting the relative proportions of highly unsaturated compounds and less highly unsaturated compounds and in subjecting said acids to an oxidation process capable of yielding a resilient adhesive and tacky product.

6. The process for the manufacture of linoleum cement from mixtures of oils containing glycerides more unsaturated than olein and fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, which consists in removing from said substances, some of the non-drying bodies contained therein, and subjecting resulting material to an oxidation process capable of yielding a resilient adhesive and tacky product.

7. The process for the manufacture of linoleum cement from mixtures of oil containing oils more unsaturated than oleins, and fatty acids derived from oils containing fatty acids more unsaturated than oleic acid, which consists in treating said acids for removal of non drying bodies by distillation and in subjecting resulting acids to an oxidation process conducted in such manner as to yield a resilient, adhesive and tacky product.

8. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in subjecting said glycerides to an oxidation process capable of yielding a resilient tacky and adhesive product.

9. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in subjecting said glycerides to an oxidation process by a gas containing free oxygen, capable of yielding a resilient tacky and adhesive product.

10. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in subjecting said glycerides to an oxidation process and in adding aluminum hydrate in such manner as to yield a resilient tacky and adhesive product.

11. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in subjecting said glycerides to an oxidation process capable of yielding a resilient tacky and adhesive product, with incorporation of rosin and suitable gums.

12. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in adjusting the relative proportions of highly and less highly unsaturated glycerides and in subjecting said glycerides to an oxidation process capable of yielding a resilient tacky and adhesive product.

13. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in treating said oils for the removal of non drying bodies by filtration and in subjecting the resulting glycerides to an oxidation process capable of yielding a resilient tacky and adhesive product.

14. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in treating said oils for removal of non drying bodies by distillation and in subjecting the resulting glycerides to an oxidation process capable of yielding a resilient tacky and adhesive product.

15. The process for the manufacture of linoleum cement from substances containing the radicals of fatty acids more unsaturated than oleic acid, (except linseed oil, tung oil or soya oil as glycerides), which consists in subjecting said acids to an oxidation process conducted at about the temperature range of 80° at first, then 100° C. to 110° C. sufficiently to yield a resilient adhesive and tacky product.

16. The process for the manufacture of linoleum cement from cotton seed oil, rape oil, cod oil or whale oil, which consists in subjecting said glycerides to an oxidation process conducted at about the temperature range of 80° at first, then 100° to 110° C. sufficiently to yield a resilient tacky and adhesive product.

17. The process for the manufacture of linoleum cement from oils containing glycerides of fatty acids more unsaturated than oleic acid mixed with free fatty acids derived from such oils which consists in subjecting said mixture to an oxidation process capable of yielding a resilient adhesive and tacky product.

18. The process for the manufacture of linoleum cement which comprises subjecting oily by-products containing the radical of a fatty acid more unsaturated than oleic acid to an oxidation process capable of yielding a resilient, tacky and adhesive product.

19. The process as claimed in claim 1 in which a fatty acid more unsaturated than oleic acid is oxidized.

In witness whereof, I have hereunto signed my name, in the presence of two subscribing witnesses.

ALFRED BREWERTON CRAVEN.

Witnesses:

ARTHUR OLDROYD,

CHARLES SAMUEL BEDFORD.