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OIL COMPOSITION AND PROCESS OF RETARDMENT DEVELOPING OF RANCIDITY THEREIN.

No Drawing.

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This invention relates to coating compositions containing an unsaturated fatty oil and a rancidity-retarder for said oil comprising an amine, particularly an aromatic amine, and includes also a process of retarding the development of rancidity in oils which have a tendency to become rancid.

The chief object of our invention is to improve upon nitrocellulose "dope" compositions for use in coating of fabrics, paper, split leathers, and in general for leather substitute uses. The invention includes a composition including a base material, a substance containing a fatty acid radical and having a tendency to become rancid, and an aromatic amine having a volatility adapting it to remain substantially permanently in the composition.

It has been customary for many years to use vegetable oils as softeners for pyroxylin compositions. For example, castor oil is very generally used in the surface film of artificial leather, and either castor oil or blown rapeseed oil is used in most of the dope applied to split leather. It is noteworthy that the oils used for this purpose belong in the class of unsaturated glycerides, and it is a well-known fact that none of the saturated glycerides is a liquid at ordinary temperature.

The most serious objection to the use of vegetable oils as softeners of pyroxylin is their tendency to become rancid. The development of rancidity in vegetable oils and fats has been made the subject of a great deal of study, and a great many contradictory conclusions have been drawn. The results of our experiments, however, agree in the main with those of the Bureau of Animal Industry, at Washington, reported by Robert H. Kerr in an article published in the July 1921 number of the "Cotton Oil Press." Mr. Kerr states that it is practically certain that only glycerides of unsaturated acids are concerned in the development of rancidity. It is important to note, therefore, that the oils which must be used as softeners for pyroxylin are necessarily the oils which are most liable to develop rancidity.

Extensive experiments have confirmed us

in the opinion that oxidation by air is the principal cause of rancidity development by the oil, that bacterial and enzymic action play no part, and that the development of rancidity is accelerated by the action of heat and light, especially the shorter wave lengths. These experiments have convinced us of the difficulty, if not impossibility, of entirely preventing the development of rancidity, so we have experimented with the object of retarding the rate of development of rancidity.

We have discovered that aromatic amines in general are capable of effecting a retardation in the development of rancidity in oils that tend to become rancid. There are, of course, great variations in the retarding power exerted by the various individual amines, some, such as diphenylamine and the nitroarylamines, being many times more powerful than, for example, aniline. This difference in the retarding effects of different amines may probably be accounted for in part by the differences in the volatilities of the amines, the simple amines, such as aniline and many of the aliphatic amines, being so volatile that they quickly escape from the composition in which they have been incorporated. In preferable accordance with our invention we use amines which are relatively non-volatile, that is are of such low volatility that they will remain in the composition substantially permanently.

Of the aliphatic amines, we have found that urea has a substantial rancidity-retarding effect, although not as powerful in this respect as some of the aromatic amines.

The invention may be illustrated by the following example:—

A series of nitrocellulose films was made up from three compositions containing about sixteen ounces of nitrocellulose, of suitable viscosity, per gallon of solvent mixture composed of twenty parts denatured ethyl alcohol (formula containing one-half gallon benzene per 100 gallons ethyl alcohol 95% by volume), fifty parts benzene, and thirty parts ethyl acetate, together with twenty four ounces of castor oil. To one composition, no addition was

made; to the other two compositions approximately 0.08 of an ounce of urea and diphenylamine, respectively, was added or approximately 0.5% of urea or diphenylamine based on the nitrocellulose used. Films were poured on glass plates using the above three dope compositions and portions of the three films were subjected to storage at 65° C. in the dark in tightly stoppered bottles. Daily tests of the samples were made by smelling with the result that the pyroxylin film without addition developed rancidity in two days; the film containing urea did not become rancid until five days, while the film containing diphenylamine did not become rancid until ten days.

In other tests, portions of the samples were exposed in closed bottles to sunlight; the film without additions turned rancid in thirty days; the film with 0.5% urea turned rancid in the same time, while the film containing 0.5% diphenylamine did not turn rancid until forty-three days.

Rancidity tests of nitrocellulose coated fabrics containing vegetable oils, together with pigments, lakes and dyes to give desired color shade, have shown that the presence of the amine retards the development of rancidity in a similar manner in which it retards rancidity development when present in the clear film without addition of pigment or coloring matters.

The relative retarding powers of various amines in oil-nitrocellulose films is shown in the Table I. The percentage of amine is based on the oil content, and the test is for rancidity development at 65° C. in the dark. The plus sign (+) indicates that the test film had not become rancid at the end of the period noted.

Table I.

Retarder.	Per cent.	Rancidity develops in—
None		2 days.
Meta-phenylene-diamine	6	16 days.
Benzidine	6	20 days.
Meta-nitraniline	6	30 days+.
Meta-nitro-para-toluidine	6	30 days+.
Para-nitro-ortho-amine-phenol	6	30 days+.
Ortho-amino-benzoic acid	0.06	19 days+.
Alpha-naphthylamine	0.06	16 days.
Butylaniline	0.06	5 days.
Nitrosodimethylaniline	0.06	6 days.

The efficacy of diphenylamine is shown by the following experiments:

Tests were made on films composed of nitrocellulose and castor oil in the ratio of one part of the former to 2.1 parts of the latter. The solvent mixture used consisted of 60 parts benzol, 20 parts ethyl acetate, and 20 parts ethyl alcohol, and the diphenylamine was added in the form of an alcoholic solution. The films were prepared by pouring the solution on glass, and stripping after the solvent had evaporated. They were

stored in closed glass bottles in an oven kept at 65° C., and were observed every day for the development of rancidity. The following results were obtained, the percentages of diphenylamine being based on the oil content of the film:

Table II.

Per cent diphenylamine.	Time for development of rancidity.
None	2 days.
.12	8 days.
.25	30 days.
1.00	50 days.
4.00	Not rancid in 4 months.

The retarding effect of the amines is not limited to compositions containing nitrocellulose in addition to the vegetable oil, but is obtained with any vegetable oil composition. For example, castor oil exposed on filter paper at an elevated temperature develops rancidity in a few days, and this development of rancidity is markedly retarded by the addition to the oil of one percent of diphenylamine.

Although secondary aromatic amines have been exemplified above only by diphenylamine and butyl-aniline, it will be understood that other relatively non-volatile secondary amines, such as ditolylamine and amyl-aniline, may be used. Also various nitro-arylamines and aromatic amino-carboxylic acids other than those specified above may be used provided they are compatible with other constituents of the composition in which their rancidity retarding action is desired.

In making the coating compositions that are to be used in the manufacture of artificial leather, in connection with which our invention has especial utility, it is customary to grind the pigment in a small amount of oil and subsequently mix it with the bulk of the oil and nitrocellulose dissolved in a suitable solvent mixture such as denatured ethyl alcohol, benzene, and ethyl acetate or acetone. The aromatic amine retarder may be incorporated in the solution of oil and nitrocellulose before the pigment-oil mixture is added thereto.

It is to be understood that our invention is not limited to retarding the development of rancidity in oils which are present in coating compositions, but is generally applicable to any oil composition which has a tendency to become rancid.

We claim:

1. A composition of matter comprising an oil having a tendency to become rancid and a diarylamine.
2. A composition of matter comprising an oil having a tendency to become rancid and more than 0.20% of diphenylamine based upon the amount of oil present.

3. A composition of matter comprising an unsaturated vegetable oil and diphenylamine.

4. A composition of matter comprising nitrocellulose, a vegetable oil, and an aromatic amine.

5. A composition of matter comprising nitrocellulose, a vegetable oil, and a relatively non-volatile secondary aromatic amine having a volatility adapting it to remain substantially permanently in the composition.

6. A composition of matter comprising nitrocellulose, a vegetable oil, and a diarylamine.

7. A composition of matter comprising nitrocellulose, a vegetable oil, and diphenylamine.

8. A composition of matter comprising nitrocellulose, a vegetable oil, and more than 0.20% of diphenylamine based upon the amount of oil present.

9. A composition of matter comprising nitrocellulose, castor oil, and an aromatic amine.

10. A composition of matter comprising nitrocellulose, castor oil, and a relatively non-volatile secondary amine having a volatility adapting it to remain substantially permanently in the composition.

11. A composition of matter comprising nitrocellulose, castor oil, and a diarylamine.

12. A composition of matter comprising nitrocellulose, castor oil, and diphenylamine.

13. A composition of matter comprising nitrocellulose, castor oil, and more than 0.20% of diphenylamine based upon the amount of oil present.

14. A coating composition for use in the manufacture of artificial leather containing nitrocellulose, a softener therefor comprising an unsaturated glyceride, and a relatively non-volatile aromatic amine having a volatility adapting it to remain substantially permanently in the composition adapted to retard the development of rancidity in said glyceride.

15. A coating composition for use in the manufacture of artificial leather containing nitrocellulose, a softener therefor comprising an unsaturated glyceride, a pigment, and a relatively non-volatile aromatic amine having a volatility adapting it to remain substantially permanently in the composition adapted to retard the development of rancidity in said glyceride.

16. A coating composition for use in the manufacture of artificial leather containing nitrocellulose, a softener therefor comprising an unsaturated glyceride, a pigment, and

between 0.25 and 4% of diphenylamine based on the oil content.

17. A coating composition as set forth in claim 14 in which the softener comprises castor oil.

18. A coating composition as set forth in claim 16 in which the softener comprises castor oil.

19. The process of retarding the development of rancidity in a composition containing an unsaturated glyceride which comprises subjecting said composition to the continued action of a diarylamine.

20. The process of retarding the development of rancidity in a composition containing an unsaturated glyceride which comprises subjecting said composition to the continued action of diphenylamine.

21. The process of retarding the development of rancidity in a composition containing nitrocellulose and castor oil which comprises subjecting said composition to the continued action of an aromatic amine.

22. The process of retarding the development of rancidity in a composition containing nitrocellulose and castor oil which comprises subjecting said composition to the continued action of diphenylamine.

23. A composition of matter comprising a solution, in a volatile solvent, of nitrocellulose, an oil having a tendency to become rancid, and a relatively non-volatile aromatic amine having a volatility adapting it to remain substantially permanently in the composition.

24. A composition of matter comprising a solution, in a volatile solvent, of nitrocellulose, castor oil, and diphenylamine.

25. A composition for use in the manufacture of artificial leather containing nitrocellulose, an oil having the tendency to become rancid, and diphenylamine.

26. A composition for use in the manufacture of artificial leather containing nitrocellulose, castor oil and diphenylamine.

27. A composition of matter comprising a base material, a substance containing a fatty acid radical and having a tendency to become rancid, and diphenylamine.

28. A composition of matter comprising a substance containing a fatty acid radical and having a tendency to become rancid, and diphenylamine.

In testimony whereof we affix our signatures.

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CERTIFICATE OF CORRECTION.**Patent No. 1,675,631.****Granted July 3, 1928, to****WALTER D. BALDSIEFEN ET AL.**

It is hereby certified that error appears in the above numbered patent requiring correction as follows: In the grant and in the heading to the printed specification, title of invention, for the words "Retardment Developing" read "Retarding Development"; 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 14th day of August, A. D. 1928.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.