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MANUFACTURE OF ANTIOXYGENIC PAPER

Sidney Musher, New York, N. Y., assignor to
Musher Foundation Incorporated, New York,
N. Y., a corporation of New York

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This invention relates to an improved paper sheet wrapping material capable of prolonging the life of packaged organic compositions and particularly when such compositions contain oxidizable glyceride oils and fats.

Flexible cellulosic paper packaging materials such as parchment, greaseproof, glassine, sulfite, etc., papers and paperboards, whether made by the sulfite or sulfate processes have substantially no protective properties with respect to organic packaged compositions. Such papers and paperboards are, however, used for the packaging of materials of the nature of butter, margarine, lard or other shortening, crackers, cookies, cakes and cookery products, milk, orange juice, candies and confections, ice cream, cheese, bacon, hams, beef, oranges, lemons and other citrus fruit, corn flakes, wheat flakes, shredded wheat, nuts, potato chips, etc., all of which are subject to oxidative deterioration and development of objectionable off-odors and off-flavors during normal storage or distribution.

In addition, the entrained air in the package readily accelerates this deterioration for it is not practicable, where cellulosic packaging materials are used, for the packaged product to be held under vacuum or under inert gases such as nitrogen, carbon dioxide, etc.

An object of this invention is, therefore, the production of improved paper packaging materials which will prolong the life of packaged organic compositions and which will be readily acceptable for use in conjunction with food compositions and without the objection of adding foreign materials to the oxidizable food products.

Still further objects and advantages will appear from the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with this invention, it has surprisingly been found that where certain materials are applied to paper pulp before final conversion into the finished paper and where the finished paper in aqueous dispersion has a pH of between 4 and 6.9 and preferably between 5 and 6, that the finished paper or paperboard serving as the food wrapper will substantially balance the effects of the air and naturally oxidizable characteristics of the packaged organic composition.

It has, furthermore, been surprisingly found

that this protection can even be secured where only the edges of the packaged compositions are in contact with the treated paper material, the major portion of the surface of said packaged composition being in contact with air. For example, less than 10% of the total surface area of the packaged composition may be in contact with the sheet packaging material and 90% or more in contact with air, but stabilization against oxidative deterioration is nevertheless obtained.

In accomplishing the results of this invention, before the paper is completely compacted and before the pulp is finally converted into paper, there are preferably applied to the paper pulp certain di-substituted benzenes, the substances most satisfactorily employed being the hydroxy di-substituted benzenes, preferably in para position, and less preferably the hydroxy di-substituted naphthalenes. As a general rule, these substances should contain not more than 14 carbon atoms and preferably not over 10 carbon atoms.

Apparently these compounds form some combination with the cellulose of the paper packaging materials, such combination being of a physical or chemical nature, with the result that the combination of the paper material and the aromatic compound has been activated to develop marked antioxygenic and stabilizing activity.

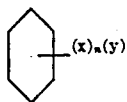
In applying these aromatic compounds to the paper pulp packaging material, it has been found most suitable to apply them so that the aromatic compound becomes an intimate part of the paper mass and is inherently and integrally associated with the cellulose fibers, applying these aromatic compounds to the paper mass desirably in aqueous suspension or solution.

The stabilizing aromatic compounds are preferably applied in amounts ranging from 0.0001% to 1% against the weight of the paper mass. Generally, about 0.005% to 0.05% by weight is the desired amount to give satisfactory protection.

The preferred aromatic hydroxy compound to use in accordance with this invention is hydroquinone. Other useful di- and tri-hydroxy compounds, the hydroxy groups of which may have been etherized, include guaiacol, phloroglucinol, resorcinol, pyrogallol, pyrocatechol, tri butyl catechol, vanillin, and similar compounds. Thymal, although a monohydroxy compound, may also be used.

These aromatic compounds are preferably those which have a single aromatic ring, desirably the phenyl ring and with the hydroxy group in the para position.

Still other less preferable useful compounds are included in the general group having the formula



where x is at least one OH and preferably may represent two OH groups or even alkoxy-groups and may less preferably include NH_2 or COOH or CHO or alkyl side chains containing the same; where n is at least 2; and where y is hydrogen, aryl, alkoxy, aralkyl, alpharyl, amino, or alkyl chains or groups including the same.

The treated paper or paperboard mass is desirably adjusted to a pH of 4 to 6.9 and preferably to a pH of 5 to 6. The pH adjustment is important in order to obtain the maximum stabilizing results of the present invention. Where the pH is above 7.0, the protective effects normally exerted is very substantially reduced.

The pH adjustment is made desirably by the use of an inorganic acid such as hydrochloric acid or sulfuric acid. The pH adjustment may be made in any desired way such as to the paper stock or mass in the beaters or subsequently in the forming operation.

The hydroquinone is applied to the paper mass so that it is particularly present on the surface of the mass and desirably spread out in a thin film on that portion of the surface which is subsequently to be placed into contact with the edges of the oxidizable packaged products.

As an example of the method by which the hydroquinone or similar aromatic compound may be applied, it may be added to the tubs through which the paper or paperboard passes, using from 0.05% to 5% of the hydroquinone against the weight of the water and other materials contained in the size. About 0.1% to 1% of hydroquinone against the weight of the water in the trough is a satisfactory amount. When the paper mass, whether it be the mass of the parchment paper, sulfite paper, greaseproof paper, glassine paper, prime stock or secondary stock paperboard, passes through the trough containing the hydroquinone, sufficient of the hydroquinone will become part of the paper mass to give marked stabilizing activity to packaged organic compositions.

The hydroquinone may be applied to the paper mass along with non-oxidizing substantially neutral materials and particularly with hydroxylated aliphatic compounds as these aid most satisfactorily in obtaining the desired results. Such other materials include glycerine and its related compounds, carbohydrates such as starch and sugars, dextrin and carbohydrate gums such as gum arabic, gum karaya, gum tragacanth, etc. and also proteins, preferably of high molecular weight, such as casein, soya protein, partly or wholly coagulated gelatin or glue. There may also be present in the trough wax sizes or wax sizing emulsions such as rosin wax sizes.

A particularly desirable method for the application of the hydroquinone to the paper mass is first to admix it with a carrier as indicated above. For example, to the tapioca or corn starch there may be added from 0.5% to 5% by weight of hydroquinone and the combination thoroughly mixed. Where desired, the starch may then be boiled or treated with an enzyme to prepare for addition to the troughs for application to the paper mass.

Desirably, the paper or paperboard mass may

be allowed to pass through the trough containing the solution of the hydroquinone in water so that the surface of the paper or paperboard picks up some of the hydroquinone solution.

The process of the present invention is most particularly of value in connection with the plain (non-regenerated) types of papers and paperboards whereby no hard surface film is present. Where a hard surface film of the nature of the regenerated cellulosic films, resinous sizing materials, etc., is utilized, the results of the present invention are not readily obtained and most desirably, the treatment of the present invention should be given to ordinary absorbent paper and paperboard.

Surprisingly, it has been found that the treatment of paper with hydroquinone in the manner indicated will show even better results than where the same amount of hydroquinone is added to the packaged composition.

Example I

A mixture was prepared comprising 1% of hydroquinone and 99% of tapioca starch by weight. The starch-hydroquinone combination was gelatinized by boiling in 7 times its weight of water and then sufficient additional water was added so that only 6% of the gelatinized starch-hydroquinone combination was present in the water. There was also added to the bath 0.1% of hydrochloric acid. Paperboard mass made of second grade sulphite stock was passed through this bath and the board was then heated to 220° F. until thoroughly dry. The board thus made was used for the packaging of sweet wafers, only the edges of which touched the board. The wafers thus packaged were found to be extremely resistant to rancidity and to the development of carton odors and tastes.

The protection afforded is of particular value in view of the fact that the addition of hydroquinone to crackers would be prohibited because of the questionable edibility of that product whereas, in accordance with this invention, the hydroquinone may be utilized without question by food authorities.

Furthermore, it is not well understood as to why the presence of hydroquinone on the paper should be so much more effective than where it is directly added to and dispersed in the packaged composition.

In the case of those papers that are sized or coated with wax, paraffin, paraffin or petrolatum oils, hydrogenated fat or similar surface coatings of non-resinous character, the hydroquinone is desirably applied to the paper or paperboard mass in the tub sizing bath and the paper or paperboard then waxed, paraffined or oil impregnated, and such paper or paperboard will retain its protective properties in the same way and even in a more effective way than if the hydroquinone has been mixed with the paraffin or paraffin oil.

Surprisingly, the paraffin or wax covering over the hydroquinone whereby the hydroquinone is kept from contact with the packaged composition presents no barrier to giving substantial protection to packaged oil or fat containing organic compositions. Such papers or paperboards may, after the treatment of the hydroquinone therewith, be surface coated with paraffin or impregnated with paraffin oils and utilized in the packaging of milk, orange juice, meats, fish and poultry for storage, biscuits and crackers, caramels and candies, etc.

The treatment of paper packaging materials

with hydroquinone before the waxing thereof is of particular importance because there is avoided any possibility of contact between the packaged organic composition and the hydroquinone due to the paraffin layer. Even though, therefore, the stabilizer used be objectionable if it were to contact the packaged composition such as if hydroquinone or pyrogallol were to be in intimate contact with a packaged food product, and even though such objectionable stabilizer were not in direct contact with the packaged food product to contaminate it, nevertheless the hydroquinone or pyrogallol under the paraffin film substantially stabilizes that packaged food product. Similarly, it is also possible to use latex or similar rubber composition as an overcoat over the antioxygenic film.

It is particularly desirable to subject the paper or paperboard following the application thereto of the hydroquinone solution to an elevated temperature of at least 210° F. and preferably to 220° F. or above. Under the conditions of the elevated temperature, the hydroquinone becomes much more effective, which increase in effectiveness is particularly noticeable in the treatment of boards of low quality stock such as of pine board which is so readily susceptible to transferring objectionable cardboard odors to packaged compositions.

Example II

A mass of paperboard made of pine stock was treated with hydroquinone by passing it through a bath containing 10% of hydroquinone by weight. Part of the board mass thus treated was dried in a vacuum oven at 135° F. and part subjected to a temperature of 220° F. until dried. The boards were then used for the packaging of sweet cookies and held at 98 F. in the dark. It was observed that the cookies packed in the board which was dried at 220° F. kept free of the objectionable "cardboard" odor and flavor for about 40% longer than the cookies packed in the board which was dried at 135° F.

It is not known as to why the heat treatment should so definitely increase the stabilizing value of the aromatic compositions described for it would normally be expected that the treatment decrease the effectiveness of the stabilizer. Apparently, however, some reaction occurs whereby the effectiveness of the hydroquinone or similar materials is definitely enhanced by the heat treatment.

It is particularly desirable, therefore, in accordance with the present invention for the hydroquinone or similar aromatic materials to be applied to the calender stacks or to become impregnated with the paper mass by permitting the paper or paperboard mass to pass through a trough containing the hydroquinone or similar materials, and for the paper or paperboard of at least 210° F. and preferably at 220° F. or higher.

Where desired, the pH adjustment may be made in the same trough containing the hydroquinone and, in addition to the various acids that may be used for the pH adjustment, alum may also be employed.

A particularly desirable method of treatment of the paper and paperboard mass is for the hydroquinone in aqueous suspension or solution to be sprayed or allowed to flow on the moving sheet of paper or paperboard mass at the wet end of paper machine and immediately before such paper or paperboard come in contact with the heated drying rolls.

By this means, there may be applied to the

paper or paperboard mass a controlled quantity of the hydroquinone as the amount applied will not be dependent upon the amount that is picked up by the paper or paperboard mass as would be the case where the paper mass passes through the trough containing the hydroquinone.

The hydroquinone is applied to and becomes a part of the paper mass in a substantially invisible and inappreciable form.

The hydroquinone may much less desirably be added to the beaters but it has been observed that when the addition is made to the beaters, no more than 50% and in most cases much less effectiveness is obtained than where the paper mass is treated after having been partially formed. In the case of the low grade second grade stock boards, and particularly in the treatment of paperboard made of pine stock and other low grade board, the hydroquinone may be applied to the beaters.

The hydroquinone or similar material used in accordance with this invention does not work on the principle of absorbing light rays responsible for the oxidative deterioration of packaged organic compositions and the paper or paperboard made in accordance with this invention is primarily intended for utilization in the packaging of foodstuffs that are held on grocery store shelves or under refrigeration where they would not be exposed to such objectionable light rays allegedly responsible for rancidity of fats exposed to them.

As stated above, the preferred compounds utilized are absorbed and become part of the paper sheet material without causing any substantial change in the color or appearance thereof and the stabilizing activity which is obtained appears to arise from catalytic chemical contact action without any light filtration or direct combination with the packaged composition, although there may be a combination with the paper or board of polyhydroxylated aliphatic materials utilized as carriers to give enhanced benefit.

Although it is usually desirable to utilize the hydroquinone or other aromatic compound by itself, for treatment with the paper mass, it is also possible to use combinations of the aromatic compounds with lecithin, kephalin, phosphoric acid, phosphatides, glucose, sucrose, lactose or other sugars, and less preferably with the alkali metal phosphates, calcium phosphates, tartaric, citric or other polybasic and/or polyhydroxy aliphatic acid, this combination being utilized particularly in the treatment of second grade stock papers and paperboards such as paperboard made of pine stock and where the paper is subjected to an elevated temperature of at least 210° F. and preferably to 220° F. or above after the application of the combination thereto. These added compounds may generally be used in amounts ranging from 5% to 100% of the hydroquinone used.

Together with or in lieu of the aromatic antioxygenic materials, there may less preferably be employed the aliphatic polycarboxylic acids and particularly their sodium or potassium salts. Sodium citrate is one of the preferable compounds to be used in this series, but these materials are very much less desirable and do not give the results shown by the aromatic antioxygenic compounds and particularly the disubstituted benzenes particularly set forth in the present application.

By the expression "secondary" as used in con-

nection with secondary board is meant paper-board made from once used or second grade paper stock as used by the paper manufacturers. "Pine board" or "pine stock board" is intended to include paper or paperboard made from pine stock or pine pulp which contains a small amount of pine oil and other impurities readily subject to oxidative deterioration.

Having described my invention, what I claim is:

1. A method of making an antioxygenic paper, which comprises adding to a paper pulp an aqueous dispersion containing between 0.05% to 5% of an aromatic antioxygenic compound, the paper pulp and the dispersion both having a pH of about between 4 and 6.9, and then compacting the paper pulp at an elevated temperature of over about 210° F. to form the paper and to cause such aromatic antioxygenic compound to become an integral part of the paper, said aromatic compound being selected from the group consisting of hydroquinone, guaiacol, phloroglucinol, resorcinol, pyrogallol, pyrocatechol, tri butyl catechol, and vanillin.

2. In the method of making antioxygenic paper the steps of providing paper pulp with a pH of between 4 and 6.9, adding to the paper pulp a small amount, less than 1%, of hydroquinone while maintaining a pH between 4 and 6.9, and then compacting the paper pulp at a temperature of at least 210° F. to form the paper and to cause the hydroquinone to become an integral part of the paper.

3. In the method of making antioxygenic paper the steps of providing paper pulp with a pH of between 4 and 6.9, adding to the paper pulp a small amount, less than 1%, of an aromatic compound while maintaining a pH between 4 and 6.9, and then compacting the paper pulp at a temperature of at least 210° F. to cause a reaction between the aromatic compound and the paper pulp and to form the antioxygenic paper, said aromatic compound being selected from the group consisting of hydroquinone, guaiacol, phloroglucinol, resorcinol, pyrogallol, pyrocatechol, tri butyl catechol, and vanillin.

4. In the method of making antioxygenic paper, the steps of providing paper pulp with a pH of between 4 and 6.9, adding to the paper pulp a small amount, less than 1%, of a combination of an aromatic antioxygenic compound and a material selected from the group consisting of the phosphatides and phosphoric acid while maintaining a pH between 4 and 6.9, and then compacting the paper pulp at a temperature of at least 210° F. to cause a reaction between the combination and the paper pulp and to form the antioxygenic paper, said aromatic compound being selected from the group consisting of hydroquinone, guaiacol, phloroglucinol, resorcinol, pyrogallol, pyrocatechol, tri butyl catechol, and vanillin.

5. In the method of making antioxygenic paper, the steps of providing paper pulp with a pH of between 4 and 6.9, adding to the paper pulp a small amount, less than 1%, of a combination of hydroquinone and a material selected from the group consisting of the phosphatides and phosphoric acid while maintaining a pH between 4 and 6.9 and then compacting the paper pulp at a temperature of at least 210° F. to cause a reaction between the combination and the paper pulp and to form the antioxygenic paper.

6. In the method of making antioxygenic paper, the steps of providing paper pulp with a pH of between 4 and 6.9, applying to the surface of the paper pulp a small amount, less than 1%, of an aromatic compound while maintaining a pH between 4 and 6.9, and then compacting the paper pulp at a temperature of at least 210° F. to cause a reaction between the aromatic compound and the paper pulp and to form the antioxygenic paper, said aromatic compound being selected from the group consisting of hydroquinone, guaiacol, phloroglucinol, resorcinol, pyrogallol, pyrocatechol, tri butyl catechol, and vanillin.

SIDNEY MUSER.