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STABLE EMULSIONS

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This invention relates to antioxidant compositions useful in papermaking and to a process for employing such emulsions in paper manufacturing. More particularly, it relates to novel antioxidant emulsions and their application to paper during manufacture.

The addition of chemical stabilizers, preservatives or antioxidants to organic materials subject to oxidative deterioration is well known. Small amounts of antioxidants have been incorporated into such materials as butter, lard, hydrogenated fats, vegetable oils and the like, as well as into toilet soaps and other non-food items. In the case of foods, of course, the antioxidant must be non-toxic as well as tasteless and non-discoloring. Antioxidants used in such materials as soaps, which contact the human skin, must be non-toxic, non-irritating and non allergenic. Thus, severe restrictions apply to properties of chemical antioxidants or oxidation inhibitors which are to be incorporated directly into the organic material to be stabilized.

In most organic materials packaged in solid form, such as butter or soap, oxidative attack occurs mostly at the surface of the material. As a consequence, it is more important to provide the antioxidant at the surface than in the bulk of the packaged item. Thus, more economical use of the antioxidant can be made if the antioxidant is employed only at that surface. This employment is conventionally carried out by incorporating the antioxidant in the paper packaging surrounding and in contact with the packaged item. Since it is known that paper, or traces of chemicals in the paper, catalyze the oxidation of fats and oils, the inclusion of antioxidant in the paper serves both to protect the packaged item in general and to repress the oxidative effect of the paper in particular. Since in oily materials, such as butter, oil leached from the packaged item into the packaging paper tends to turn rancid rapidly because of the nature and extended surface of the paper, the incorporation of antioxidant in the paper also prevents such rancidity from developing.

A variety of methods have been employed for impregnating paper with antioxidants. Typical methods include the addition to the paper of antioxidant emulsions at the beater, or as emulsion or solutions to the finished sheet leaving the Fourdrinier machine. The latter type of application may be accomplished by passing the sheet through a bath of the antioxidant-containing liquid or by calendering the liquid onto the paper. In either case, the dispersant or solvent liquid must be removed from the paper sheet in the course of manufacture. Such removal is generally accomplished by passing the paper over steam-heated dryer rolls which remove not only much of the water in the moving sheet but also any other volatile liquids which have been added to the paper in the course of manufacture.

It has been observed that serious antioxidant losses occur when impregnated papers containing conventional phenolic stabilizers are passed through heated drying sections of papermaking machines. Losses as great as 90% of the added stabilizer have been measured. As a consequence, to obtain given concentrations of antioxidant in certain papers, ten times as much of the compound must be added thereto. Since antioxidants are generally expensive chemicals, losses on such a scale seriously increase the cost of the impregnated paper.

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The loss of antioxidant has been found to result not from the volatility of the antioxidant alone but from its steam distillation thereof when wet paper containing the stabilizer is dried under the conditions described. Under the conditions of paper drying, the partial vapor pressure of the relatively non-volatile phenolic antioxidant in the stream is sufficient to effect the rapid removal of the antioxidant from the paper with the removal of the water of manufacture in the paper.

It has been found that by employing the antioxidant in the form of an emulsion in certain non-volatile water-immiscible liquids the loss of antioxidant by steam distillation is effectively prevented. As a consequence, it is an object of this invention to provide an antioxidant composition which, when employed in paper, will reduce or prevent loss of the antioxidant. A further object is the provision of a non-toxic antioxidant composition which may be employed in paper used in the packaging of foods, soap and other items intended for human consumption and use. The provision of an economical composition for such purposes which may be conveniently used in papermaking is another object of the invention. Still another object is the provision of a process for employing the antioxidant compositions of the invention. Other objects will be clear from the following description of the invention. Another object is the provision of an emulsion which is unusually easy to prepare and is remarkably stable.

These objects are accomplished in the invention by a stable aqueous emulsion consisting of a continuous aqueous phase having dispersed therein an oil phase consisting of a water-immiscible ester selected from the group consisting of diisobutyl phthalate and ethyl hexyl diphenyl phosphate, up to 100% by weight, based on the ester, of 2,6-di-tert-butyl-4-methylphenol, and up to 100% by weight, based on the phenol, of a fatty acid ester of polyoxyethylene sorbitan. This emulsion has the advantage of being very easily prepared, extremely stable, and being entirely composed of components which are safe for human consumption.

Of the many phenolic antioxidants known, one of the most effective single compounds is 2,6-di-tert-butyl-4-methylphenol. This compound is also known as butylated hydroxytoluene and as di-tert-butyl-p-cresol. Because it is one of the few synthetic chemical compounds approved for antioxidant use in foods by the Food and Drug Administration, it is employed extensively in foods and food packaging.

The 2,6-di-tert-butyl-4-methylphenol is employed in the composition of the invention as a solute in a special type of non-volatile ester. This type of ester has been approved for food packaging by the U.S. Food and Drug Administration and is selected from diisobutyl adipate and ethyl hexyl diphenyl phosphate. In addition to being suitable for food uses, both of these esters have extremely low vapor pressure at relatively high temperature. The boiling point and vapor pressure of ethyl hexyl diphenyl phosphate, for example, are shown in the following table:

Temperature, °C.....	160	200	225	250	374
Vapor pressure abs., mm. Hg.....	0.1	1.3	3.5	10	760

while the boiling point of diisobutyl adipate is 282° C. Both esters are also excellent solvents for 2,6-di-tert-butyl-4-methylphenol.

The proportions in which the solvent ester and the antioxidant 2,6-di-tert-butyl-4-methylphenol may be employed vary widely. Amounts of the antioxidant up to 100% by weight, based on the ester, give satisfactory results, although slightly lower amounts, on the order of 60-80% by weight, on the same basis, have been found

to be optimal and are therefore preferred. In general, the amount employed most conveniently is the maximum soluble in the ester at room temperature, although it is obvious that by using higher temperatures more antioxidant may be dissolved in the ester. The limits of solubility of the antioxidant in several solvents at 21° C. are tabulated below:

	Corn Oil	White Refined Mineral Oil	Ethyl Hexyl Diphenyl Phosphate	Diisobutyl Adipate
2,6-di-tert-butyl 4-methylphenol solubility at 21° C. (g./100 g.).	30	30	60	80

From these data it will be apparent that far more of the antioxidant can be incorporated in paper with a given amount of the esters of this invention than can be when corn or mineral oil is employed.

The ester solution of 2,6-di-tert-butyl-4-methylphenol is dispersed in water to form the emulsion of the invention. The dispersion may be accomplished by any of the means known to the art, such as shakers, stirrers, colloid mills and the like. The amount of water employed for the dispersion is, of course, at least that required to form a continuous phase and may be as little as 10% by volume, based on the ester. The quantity of water required will, however, depend on such variables as the temperature of the dispersion and the nature of the emulsifying agent employed.

To stabilize the oil-in-water dispersion of the ester containing the antioxidant in the water, an ester-miscible emulsifier is employed. These emulsifiers are selected from the polyoxyethylene sorbitan esters of fatty acids having 12 to 18 carbon atoms. Example of such esters include polyoxyethylene sorbitant monolaurate, polyoxyethylene sorbitant monopalmitate, polyoxyethylene sorbitan monostearate, and polyoxyethylene sorbitan monooleate. Of these esters, that which has been found to afford the most stability is polyoxyethylene sorbitan monooleate, and it is therefore the preferred emulsifier. While the emulsifier may be employed in a concentration of up to 100% by weight, based on the weight of 2,6-di-tert-butyl-4-methylphenol in the emulsion, about 10-30% by weight has been found to be sufficient under most conditions.

One principal advantage of the emulsions of the invention is the ease with which they are formed. It has been unexpectedly found that merely by adding the ester solution containing the phenol and emulsifier to water and stirring the mixture extremely stable oil-in-water emulsions are almost instantly formed. These emulsions are not broken upon heating, dilution, or agitation, and thus are particularly suitable for use under industrial conditions where ease of preparation and considerable stability are desired.

Such an emulsion affords a useful concentrate which can be prepared, stored and transported without breaking, and which may be readily diluted with additional water prior to use. In practice, the diluted emulsion, in any desired concentration, is applied to paper by rolling, brushing or spraying the preparation onto the moving sheet. Since the sheet will then contain the water from the continuous phase of the emulsion as well as water from the papermaking process itself, the water is best removed by passing the sheet to the drying section of the papermaking machine and driving off the water at that stage.

By "paper" in this description is meant not only unwaxed paper and glassine paper but also waxed papers wherein the emulsion may be added to the paper prior to coating, and paperboard including waxed paperboard and such unwaxed board as chocolate board. The use of the emulsion described with these types of paper and paperboard will in no way limit the incorporation in or

on the paper or board of conventional paper additives, such as wax; glue, starch and other sizes; clay, talc, chalk and other fillers; titanium or zinc oxides and other pigments; and inks or other coatings. Furthermore, the paper packaging materials prepared with the emulsion described may be used alone or with a protective outer wrapping of cellophane, metal foil such as aluminum foil, synthetic organic resins such as polyethylene or polystyrene, and the like.

The following examples will illustrate the nature and advantages of the invention. It should be understood, however, that the examples are merely illustrative and are not to be regarded as limitations to the appended claims since the basic teachings thereof may be varied at will as will be understood by one skilled in the art.

Example I

An oil-in-water emulsion was prepared in which the oil phase had the following composition:

	Parts by weight
2,6-di-tert-butyl-4-methylphenol	10.0
Diisobutyl phthalate	12.5
Tween 80 (polyoxyethylene sorbitan monooleate)	2.5
Total	25.0

This ester solution was stirred into water until the total emulsion contained 6% w. of the phenol in the organic dispersed phase. The emulsion formed readily on hand-stirring.

Similar emulsions are formed by substituting ethyl hexyl diphenyl phosphate.

In a plant run, twelve tons of paperboard were impregnated with the emulsion, the level of impregnation being about two pounds of the phenol per ton of paperboard.

Samples of the paperboard were taken at various times during the run, and a sample of the emulsion was analyzed at the beginning of the run. Resulting data are presented in the following table:

Sample	Average percent w., 2,6-di-tert-butyl-4-methylphenol
Starting emulsion	0.6
Initial paperboard	0.07
Middle paperboard	0.14
Final paperboard	0.08

Samples of the treated board, together with samples of untreated board, were evaluated in an oxygen absorption test. In the test, 0.2 gram of paperboard, immersed in 1.0 gram of methyl linoleate, was stored in an oven at 50° C. The sample was weighed daily and when an increase of 12 mg. was obtained, the sample was considered rancid. Results of the test are given below.

Sample	Days to Rancidity at 50° C.
No paperboard	7
Untreated board	3 1/4
Initial board	5 3/4
Middle board	8
Final board	5 3/4

Example II

Two 10-ml. samples of organic antioxidant solutions were emulsified. The first solution had the following composition:

	Parts by weight
2,6-di-tert-butyl-4-methylphenol	10
Diisobutyl adipate	12.5
Tween 80 (polyoxyethylene sorbitan monooleate)	2.5
Total	25.0

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This solution was added to about 250 ml. of water and the mixture was stirred gently with a glass stirring rod. A white emulsion quickly formed which was still stable and unbroken after standing ninety days at room temperature.

When the emulsion was prepared by mixing a colloid mill at 60° C., the emulsion was still stable and unbroken after nine months standing at room temperature.

Further experiments showed that the aqueous emulsion could be quickly formed with all proportions of organic and aqueous phases merely by gentle hand stirring.

The second organic antioxidant solution had the following composition:

	Volume percent
Diisobutyl adipate.....	41.6
2,6-di-tert-butyl-4-methylphenol	20.8
Butylated hydroxyanisole	20.8
Glyceryl monostearate.....	16.7

When this solution was added to 250 ml. of water, under the above conditions, no stable emulsion could be formed by hand stirring or stirring with a conventional laboratory stirrer. The emulsion formed by such stirring broke as soon as stirring was stopped. In order to form stable emulsions, violet agitation in a colloid mill for about a half hour was required.

The aqueous emulsions formed by the mill were considerably less stable than those prepared from the first solution, breaking after about one-half the storage time.

I claim as my invention:

1. A stable aqueous emulsion consisting of a continuous aqueous phase having dispersed therein an oil phase consisting of a water-immiscible ester selected from the group consisting of diisobutyl adipate and ethyl hexyl diphenyl phosphate, from about 60% to 100% by weight, based on the ester, of 2,6-di-tert-butyl-4-methylphenol, and from about 10% to 100% by weight, based on the phenol, of a fatty acid ester of polyoxyethylene sorbitan, said fatty acid having from 12 to 18 carbon atoms.

2. A stable aqueous emulsion consisting of a continuous aqueous phase having dispersed therein an oil phase consisting of diisobutyl adipate, from about 60% to 100%

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by weight, based on the adipate, of 2,6-di-tert-butyl-4-methylphenol, and from about 10% to 100% by weight, based on the phenol, of a fatty acid ester of polyoxyethylene sorbitan, said fatty acid having from 12 to 18 carbon atoms.

3. A stable aqueous emulsion consisting of a continuous aqueous phase having therein an oil phase consisting of ethyl hexyl diphenyl phosphate, from about 60% to 100% by weight, based on the phosphate, of 2,6-di-tert-butyl-4-methylphenol, and from about 10% to 100% by weight, based on the phenol, of a fatty acid ester of polyoxyethylene sorbitan, said fatty acid having from 12 to 18 carbon atoms.

4. The emulsion of claim 2 wherein the fatty acid ester is polyoxyethylene sorbitan monooleate.

5. A stable aqueous emulsion consisting of a continuous aqueous phase having therein an oil phase consisting of 50% by weight of diisobutyl adipate, 40% by weight of 3,5-di-tert-butyl-4-methylphenol, and 10% by weight of polyoxyethylene sorbitan monooleate.

6. A process for impregnating paper with an antioxidant, comprising applying to the paper an aqueous emulsion consisting of a continuous aqueous phase having dispersed therein an oil phase consisting of a water-immiscible ester selected from the group consisting of diisobutyl adipate and ethyl hexyl diphenyl phosphate, from about 30% to 100% by weight, based on the ester, of 2,6-di-tert-butyl-4-methylphenol, and from about 10% to 100% by weight, based on the phenol, of a fatty acid ester of a fatty acid ester of polyoxyethylene sorbitan, said fatty acid having from 12 to 18 carbon atoms.

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