Patented June 9, 1936 2,043,860

UNITED STATES PATENT OFFICE

2,043,860

PRESERVATION OF SUBSTANCES

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No Drawing. Application March 14, 1934, Serial No. 715,431

10 Claims. (Cl. 99—163)

This invention relates in general to the preservation of light-unstable oils, fats and waxes and substances containing the same. In particular, it relates to an improved article or element for protecting such substances from the action of light, including the ultra-violet rays, and includes correlated improvements and discoveries whereby the stability and desirable characteristics thereof are enhanced.

It is known that light-unstable oils, fats and waxes undergo certain undesirable changes resulting in the condition commonly designated by the term "rancid" or "tallowy" upon exposure to certain agents such as oxygen, metals and light. With regard to the role that light plays in the development of rancidity, the literature is incomplete and full of contradictory statements, in consequence of which many unsatisfactory types of protective elements have been proposed for retarding the rancidity of oils, fats and waxes.

For example, it has long been proposed to preserve light-unstable oils, fats and waxes or substances containing the same by enclosing them in containers which are completely opaque, such as metal foil and black glass. From a commercial viewpoint, these opaque containers are unsatisfactory in making it impossible for one to see the contents of the container, so that the container must be opened in order to judge the nature or condition thereof. It has also been suggested to employ dark colored containers for these substances, but here again the object of using such color has been to achieve a general reduction of light transmitted and no regard was given to whether light other than visible was transmitted and to the possible effect of such light on the development of rancidity.

In U. S. Patent No. 1,880,813 it is disclosed that "green or black protective materials or the foils are effective in preventing or retarding the progress of rancidity, while transparent protective materials of red, pink, blue or orange are not effective in this respect, and further, that purple or yellow transparent containers catalyze the photochemical reaction resulting in rancidity". In said patent it is proposed that containers be employed "which admit only wave lengths of light lying between 4900 and 5600 Angstrom units (A. U.) of the spectrum", this region being indicated as having no effect in the development of rancidity.

From a practical standpoint, the green wrapper of the aforesaid patent permits the transmission of a very narrow region of the visible spectrum, viz., 4900 to 5600 A. U., thus restricting the coloring matters which may be utilized in the protective screen. From a commercial standpoint, a green protective element is not suitable for displaying many types of merchandise which, owing to their own color, do not appear attractive and cannot be adequately distinguished when displayed under such an element. Accordingly, there is a real need for a protective element which shows not only the retardation of rancidity, but also a high degree of transparency to visible light of a wide range of the spectrum.

It is a general object of the invention to provide a process for preserving light-unstable oils, fats and waxes and substances containing the same by shielding them from the action of light capable of promoting the rancidity of such substances, while permitting transmission of various wave lengths of visible light so that the wrapped article may be clearly seen through the wrapper.

It is a further object of the invention to provide, as an improved article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same whereby the development of rancidity in such substances may be substantially retarded while permitting the use of a wide freedom in the nature of light transmitted by the element for the purpose of displaying said substances for visual examination.

It is a specific object of the invention to provide, as an improved article of manufacture, a formed container for preserving light-unstable oils, fats and waxes characterized by being substantially opaque to light capable of promoting the rancidity of such substances.

Another specific object of the invention is to provide a wrapping material for preserving light-unstable oils, fats and waxes characterized by being substantially opaque to those wave lengths of light which are capable of promoting the rancidity of such substances and being, in addition, of a color selected from the group consisting of red, orange and yellow.

A still further object of the invention is to provide a novel and improved article of manufacture consisting of a material containing light-unstable oils, fats and waxes enclosed in a protective wrapper, the wrapper being substantially opaque to those wave lengths of light which are capable of promoting the rancidity of the oils, fats and waxes and being substantially transparent to various wave lengths of visible light.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises a novel

article comprising the elements and the relation of elements, and a process comprising the steps and the relation of steps, all as exemplified in the following detailed disclosure and the scope of the invention will be indicated in the claims.

I have found that, in general, the rancidity of light-unstable oils, fats and waxes and substances containing the same is promoted by light having wave lengths of from about 2900 to 4700 A. U. I have found, further, that contrary to the teachings of the aforesaid patent, it is not essential in retarding the rancidity of light-unstable oils, fats and waxes to exclude all light above 5600 A. U. and in particular that yellow light alone does not catalyze the photochemical reaction resulting in rancidity.

In the practice of the invention a protective element for light-unstable oils, fats and waxes is formed from a material characterized by being substantially transparent to or non-absorbent of light having a wave length other than 2900 to 4700 A. U. to which wave lengths it is substantially opaque, or from a material that has been combined, impregnated and/or coated with a substance substantially absorbent of or opaque to light of said wave lengths. The protective element is also characterized by effecting a retardation of rancidity of said oils, fats and waxes for a period at least four times that of such substances unprotected by said element. The expression "substantially opaque" as used throughout the specification and claims connotes a transmission not greater than 25% of the incident light of any one wave length in the region 2900 to 4700 A. U. and a total transmission not greater than 10% within this region.

It cannot be foretold whether or not a material having the colors red, orange or yellow is effective in retarding rancidity since it has been found that some materials having these colors afford a high degree of protection; while other materials appearing of substantially the same shade are ineffective in retarding rancidity. Therefore, the dye-stuffs and coloring matters which may be utilized in the invention are presented not only by stating the light which is transmitted by them, that is, as to whether they are red, orange or yellow, but also by specifying the factor which actually determines the effectiveness of any particular dye-stuff, that is, the absorption characteristics in the blue and ultra-violet regions of the spectrum. Suitable dye-stuffs and coloring matters for use in the invention are those which absorb appreciably or are substantially opaque in the near ultra-violet and blue regions of the spectrum defined by the wave lengths of from about 2900 to 4700 A. U.

By way of illustration, and without limiting the invention, I give below a number of coloring matters which are suitable for use. In the first column of this table is given the Society of Colorists and Dyers color index number (The Color Index, F. N. Rowe, editor, First Edition, 1924) which, with the technical name of the dye-stuff given in the second column, will serve to identify the dye-stuffs and their chemistry. The third column gives the source, in view of the fact that materials carrying the same technical name but secured from different sources frequently show considerable differences in their absorption spectra; the fourth column gives the preferred concentration of the dye-stuff in the dyeing bath, and the last column shows the primary color sensation to the human eye given by the protective element.

Concentrations indicated are those found suitable for producing rancidity-retarding sheets of regenerated cellulose .0010'' thick when dyed in a 90–100° C. bath to a maximum shade. The concentration of lead chromate is not given inasmuch as it is insoluble and the process of preparing an article containing it consists in dipping the material in a solution of 15 grams of lead acetate in 100 cc. of water; removing the excess of liquid from the surface; dipping the treated material into a solution of 15 grams of sodium chromate in 100 cc. of water, and thereafter washing in water.

It is not practicable to designate specifically the concentration to be used with each variety of supporting element inasmuch as the amount of dye-stuff absorbed will vary according to the nature and thickness thereof. The dye-stuff or coloring matter may be incorporated in the supporting element during or after the manufacture

Color index No.	Dyestuff	Source	Concentration gms./100 cc.	Color of film
812	Primuline S X Conc. lead chromate	Gen'l Dyestuff Corp.	4.00	Canary yellow
816	Direct brilliant yellow 3 GN	do	1.33	Do.
10	Naphthol yellow S	do	2.00	Pure yellow
812	Primuline	Eimer & Amend, N. Y.	6.00	Do.
6	Chrome printing yellow GGW No. 36		2.0	
813	Fastusol Yellow R T D Ex. Conc.	Gen'l Dyestuff Corp.	1.0	Golden yellow
109	Dutch yellow		1.0	Do.
410	Direct yellow 73	Gen'l Dyestuff Corp.	1.0	Do.
346	Fastusol yellow 2 G A	do	1.0	Do.
365	Chrysophenine	Eimer & Amend	1.0	Tango
236	Janus yellow G	Gen'l Dyestuff Corp.	0.5	Do.
640	Tartrazine	do	4.0	Do.
622	Stilbene yellow 3 G D Conc.	do	1.33	Do.
814	Fastusol yellow 2 R D Conc.	do	2.00	Do.
	Brilliant yellow 3 G X.	do	0.8	Do.
223	Cotton yellow R	do	2.00	Do.
948	Katigen Sulphur yellow G A	do	1.00	Do.
236	Janus yellow G	do	2.00	Orange yellow
221	Pyramine yellow R X	do	.66	Do.
364	Brilliant yellow	National Aniline Co.	.66	Do.
364	Brilliant yellow	do	1.33	Do.
221	Pyramine yellow R X	Gen'l Dyestuff Corp.	1.33	Do.
	Katigen sulphur yellow B G Ex.	do	1.00	Do.
60	Aniline brown or chrysoidin	Eimer & Amend	1.00	Orange
151	Tropaeoline 000 No. 2	do	2.00	Do.
27	Orange G	National Aniline	4.00	Do.
	Sunset yellow F C F	Gen'l Dyestuff	4.00	Do.
370	Congo red	Eimer & Amend	.33	Red
370	Congo red	do	1.33	Do.
448	Benzopurpurine	do	.4	Do.

of the latter. It is preferred that the dye-stuff be present in such a concentration that the transmission is not more than 25% of any one wave length of light between 2900 and 4700 A. U., and especially a total transmission which is not greater than 10%, and preferably less than 6% in the region between 2900 and 4700 A. U. Also, there should be not less than about 50% total transmission in the visible region from 4900 to 6900 A. U.

The supporting element may comprise materials normally translucent or transparent to visible light, such as, glass, glassine, synthetic plastics, gelatine, casein, synthetic resins of various types, non-fibrous, cellulosic materials, as regenerated cellulose, and cellulose derivatives, for example, cellulose esters, cellulose ethers, and cellulose oxy-ethers, or composite materials containing two or more of the above mentioned substances, viz., impregnated and/or coated materials, such as lacquered glass or lacquered regenerated cellulose, as well as laminated products, for example, laminated glass, paper and the like.

The novel protective element of the invention may be utilized in various forms, as protective screens, plates, caps, tubing, bands, wrapping blanks, bags and formed containers, as bottles, cartons and boxes, as well as linings for bags and formed containers.

In a preferred embodiment, the novel and improved article of the invention is in the form of a wrapper comprising a flexible sheet of transparent glycerinated regenerated cellulose combined with a suitable dye-stuff in sufficient concentration to render the sheet substantially opaque to light, having wave lengths of from about 2900 to 4700 A. U. and substantially transparent to light of a color selected from the group consisting of yellow, orange and red.

When yellow light is transmitted by the wrapper, somewhat greater visibility is obtained owing to the fact that the general visibility curve for the human eye has its maximum in the yellow region of the spectrum. Yellow is also a preferred color when the article serves as a food preserver by reason of the fact that the majority of food products are generally of a yellow color or some shade that does not clash with it.

The protective element is also characterized by retarding the rancidity of light-unstable oils, fats and waxes and substances containing the same for a period of at least four times, and preferably more than six times that of such substances unprotected, and when tested under identical conditions. Protective elements have been prepared according to the invention which protect in a ratio up to 25:1.

For the purpose of establishing a standard for comparing the protection afforded by a material combined with a light absorbing substance with one uncombined with such substances, the following test is suggested:

Similar samples of potato chips are hermetically sealed in the materials to be comparatively tested and exposed as a thin layer to the full radiation of a General Electric type S–2 sunlamp, maintaining a distance of 4½" from the tip of the lamp bulb to the sample. The exposure is made at a temperature of 35° C. for such length of time as is required for the samples of potato chips to give a Class 3 test for rancidity according to the Kreis method, and rancid by odor and taste. The samples used should give no Kreis test before exposure.

The Kreis method for testing the degree of rancidity is disclosed by Kerr in Industrial and Engineering Chemistry, 10, 471 (1918). To carry out the test, extract the oil from the potato chips with ether, filter and evaporate the ether on a water bath. Add to the ether extract an equal volume of hydrochloric acid (of sp. gr. 1.19, free of nitrosyl chloride). Shake vigorously for 30 seconds. Add to the mixture phloroglucinol solution (1% in ether) in a volume equal to the hydrochloric acid and shake again for 30 seconds— then allow the mixture to stand for 10 minutes. If a pink or red color appears in the lower acid layer, a positive reaction for rancidity is obtained, but no attention should be paid to a pale orange, yellow or faintly pink color. When a pink or red color is obtained, make a mixture of 1 part of the sample to be tested with 9 parts of liquid petrolatum and another mixture of 1 part of the sample with 19 parts of liquid petrolatum. Test as before similar portions of each of the two mixtures and note the colors.

According to the Kreis test, fats and oils may be divided into four classes, as follows: (1) those giving no reaction, (2) those giving a reaction when undiluted, (3) those giving a reaction in dilution of 1 to 10, but none in dilution 1 to 20, and (4) those giving a reaction in a dilution of 1 to 20. Class 1 represents sound oils, fats and waxes which may be expected to withstand severe exposure before turning rancid. Class 2 represents products which have not yet become rancid insofar as odor and taste are concerned, but in which those changes that will later manifest themselves as rancidity are already in progress. Class 3 represents a late stage of the incipient rancidity, the products being well advanced on the road to rancidity and, in most cases, it is evident to the senses of smell and taste. Class 4 represents those which have definitely become rancid. As above mentioned, for the object of this invention, a positive test shall be indicated by rancidity of class 3, the rancidity being definite in both odor and taste.

Where the specific characteristics of a particular dye-stuff or coloring matter indicates that the dye will not absorb at least 25% of light having a wave length of between 2900 and 4700 A. U. when used in a suitable concentration, there may be employed two or more dye-stuffs whose spectral characteristics complement each other in such a manner that the resulting dyed material has a total transmission of less than 10% and preferably less than 6% in the region 2900–4700 A. U. For example, an admixture containing orange G 1.5% and brilliant yellow .33%.

While the above remarks have applied particularly to the case in which the dye-stuff is combined, dyed or impregnated in a supporting element, the invention also contemplates employing a protective element which may be coated with a material containing a substance rendering the coating substantially opaque to light having a wave length of from about 2900 to 4700 A. U., and retarding rancidity at least four times. As an example of this embodiment of the invention, in preparing a rancidity-delaying wrapper, one may employ a sheet of regenerated cellulose or other suitable material which has been coated with a lacquer, for example, one containing nitrocellulose, a plasticizer, and a gum or resin to which has been added a suitable dyestuff in a concentration sufficient to give a product transmitting less than 25% of any light having a wave length of from 2900 to 4700 A. U. In a similar way, glass jars, bottles, or formed containers, may be

coated with a light absorbing composition as described. Where the dye-stuff is incorporated in the coating, it is, of course, necessary to employ a dye soluble in the lacquer or coating ingredients, for example, with a lacquer comprising:

Mixture A

	Percent	
Cellulose nitrate 5 sec.	59	10%
Tricresyl phosphate	10	
Diphenyl phthalate	15	
Triphenyl phthalate	15	
Paraffin wax	1	

Mixture B

	Percent	
Butyl acetate	20	90%
Ethyl acetate	20	
Toluol	60	

the following dyes have given satisfactory results:

Color Index No.	Dyestuff	Source	Concentration	Color of film
19	Oil Yellow G B	Newport Chem. Co., Passaic, N. J.	2.3	Yellow
23	Sudan Yellow GR	Gen'l Dyestuff Corp	1.8	Yellow
22	Oil Yellow AB	do	2.2	Deep yellow
-------	Sudan yellow 2 GA	do	2.0	Reddish orange

The concentration given is calculated as percentage of the other solid materials present, i. e., the mixture designated as A above.

If desired to protect the element from other agents, or to decorate the same, there may be applied a suitable coating composition. A subsequently applied coating is advantageous in enabling the use of those dye-stuffs which are characterized by "bleeding", as the coating effectively prevents the "bleeding" of the dye-stuff onto objects contacting the coating.

By the present invention there is provided a novel, protective element for light-unstable oils, fats and waxes and substances containing the same, which may be colored red, orange, or yellow, provided only that the element be substantially opaque to light having a wave length in the region lying between 2900 and 4700 A. U. Thus, there is obtained an article characterized by having a high degree of transparency to visible light, and a low degree of transparency to light causing rancidity. This affords on the one hand a wide freedom in the selection of colored light by which the materials may be displayed or observed and in the kind of merchandise enclosed in the protective element, and on the other hand, a high degree of protection against the development of rancidity in the merchandise. These characteristics make the element particularly suitable for protecting such foodstuffs as whole cereals, butter, cheese, potato chips, nuts, including peanuts; cookies, crullers, salad and cooking oils, candy and the like; also pharmaceutical preparations, liquors, cosmetics, candies, soaps, as well as the pure light-unstable oils. fats and waxes.

The expression "substantially transparent" as used in the appended claims designates a total transmission of about 50% in the visible region 4900 to 6900 A. U., and since certain changes in carrying out the above process, and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention described herein, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

I claim:

1. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, which is substantially transparent to light having a wave length other than 2900 to 4700 A. U. to which wave lengths it is substantially opaque, and by having a color selected from the group consisting of red, orange and yellow, said material retarding rancidity of said oils, fats and waxes for a period at least four times that of such substances unprotected by said protective element.

2. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, comprising a transparent material combined with a light absorbing substance, the combination so effected being substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque, the said material retarding the rancidity of said oils, fats and waxes for a period at least four times that of a material uncombined with said substance.

3. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, comprising a transparent material coated with a composition containing a light absorbing substance the coated material so obtained being substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque, and retarding the rancidity of said oils, fats and waxes for a period at least four times that of the uncoated sheet.

4. As an article of manufacture, a wrapping material for light-unstable oils, fats and waxes and substances containing the same, comprising a flexible sheet of material which is substantially transparent to light having a wave length other than 2900 to 4700 A. U. to which wave lengths it is substantially opaque, and by having a color selected from the group consisting of red, orange and yellow, said material retarding rancidity of said oils, fats and waxes for a period at least four times that of such substances unprotected by said material.

5. As an article of manufacture, a wrapping material for light-unstable oils, fats and waxes and substances containing the same, comprising a flexible sheet of transparent regenerated cellulose colored with a substance in sufficient concentration to render said sheet substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque, said sheet retarding the rancidity of said oils, fats and waxes for a period at least six times that of an uncolored sheet.

6. As an article of manufacture, a formed container for protecting light-unstable oils, fats and waxes and substances containing the same, which is substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque, and by having a color selected from the group consisting of red, orange and yellow, said material

retarding rancidity of said oils, fats and waxes for a period at least four times that of such substances when unprotected.

7. As an article of manufacture, a formed container for protecting light-unstable oils, fats and waxes and substances containing the same, comprising a material normally transparent to visible light, said material being combined with a light absorbing substance and the combination so effected being substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque.

8. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, which is substantially non-absorbent of light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque.

9. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, comprising regenerated cellulose combined with a light absorbing substance, the combination so effected being substantially non-absorbent of light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque.

10. As an article of manufacture, a protective element for light-unstable oils, fats and waxes and substances containing the same, comprising a sheet of transparent regenerated celiulose colored with a substance in a concentration sufficient to render said sheet substantially transparent to light having a wave length other than 2900 to 4700 A. U., to which wave lengths it is substantially opaque, said sheet being of a color selected from a group consisting of yellow, orange and red, and retarding the rancidity of said oils, fats and waxes for a period of at least four times that of an uncolored sheet.

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