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# STABILIZED RECONSTITUTED TOBACCO FOIL

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This invention relates to a process for stabilizing tobacco against discoloration during the manufacture of reconstituted tobacco foil and to the resulting tobacco product. More particularly it relates to pretreatment of tobacco with a liquid, hydrophobic polyoxypropylene or polyoxybutylene polyol to protect tobacco from direct contact with water during the manufacturing process. In a preferred embodiment, the hydrophobic polyol also contains an added antioxidant. The resulting reconstituted tobacco foil retains the light color of the original tobacco leaf and is suitable for use as an outer wrap for cigars, cigarillos, and similar tobacco products.

Numerous methods have been suggested for preparing reconstituted tobacco foils from finely divided or pulverized tobacco particles unsuitable for direct use in tobacco products. Such reconstituted foils must meet the general test of acceptability in taste and burning characteristics as well as have adequate physical properties such as tensile strength, dimensional stability and moisture retention. In addition, it is highly desirable, particularly for cigar outer wrappers, that the reconstituted tobacco film retain the light color of the original tobacco.

Although aqueous binder systems offer many advantages in the manufacture of reconstituted tobacco foil, the sensitivity of tobacco to water poses a serious problem to their commercial use. Not only does tobacco darken when wet with water, but the dark color remains upon drying and renders the tobacco unsuitable for use as an outer wrap. To overcome this problem, organic-soluble binder systems have been recommended in spite of the hazards associated with the use of volatile organic solvents. For example, in United States Patent 2,893,400 Detert and Buchholz describe the manufacture of tobacco foils using an organic solution of a highly substituted, organic-soluble methyl cellulose as a binder. Yet even with this system, accidental traces of water result in noticeable discoloration of the tobacco foil. Hence a simple and effective means for protecting the tobacco from direct contact with aqueous or water-containing process solutions while retaining desirable physical and smoking qualities is a useful advance in the art of preparing reconstituted tobacco foil.

It has now been discovered that tobacco can be protected from darkening through contact with water by pretreatment with a hydrophobic, liquid polyoxyalkylene diol or triol characterized by:

(1) A solubility in water of less than about 2 weight percent at 25° C.,
(2) A viscosity of 100 to 1,200 centistokes at 25° C., and
(3) An average molecular weight of from 500 to 5,000.

The resulting treated tobacco has enhanced color stability during manufacture of a reconstituted tobacco foil using a water-soluble binder. This enhanced color stability of the tobacco in contact with water is also advantageously retained by the final reconstituted tobacco product.

It has further been discovered that incorporation with the polyol during the pretreatment of the finely divided tobacco of an antioxidant in an amount sufficient to inhibit oxidation during processing permits more rapid drying of the reconstituted tobacco foil without discoloration.



Particularly suitable are sterically hindered alkylphenol antioxidants approved for food and drug use.

Treatment of the tobacco in the manner described herein does not deleteriously affect the strength of the reconstituted tobacco foil. The polyoxyalkylene polyols used are compatible with many binders generally employed in the preparation of reconstituted tobacco foil. They are essentially non-toxic and in the amounts used do not detract from the burning characteristics, flavor or other desired properties of the tobacco. While this pretreatment is particularly advantageous when a water-soluble binder is employed, it can also be used with organic-soluble binder systems wherein small amounts of water may be encountered.

Critical to the present invention is the pretreatment of the tobacco with a liquid polyoxyalkylene polyol having only limited water solubility. In practice, polyols having a solubility of 2 percent or less in water at 25° C. are satisfactory. Furthermore, to achieve ready intermixing and coating of the tobacco particles without use of a solvent or diluent, the liquid polyols should have a viscosity of about 100–1,200 centistokes at 25° C. These properties are obtained with commercial polyoxyalkylene polyols prepared by condensation of propylene oxide and/or 1,2-butylene oxide with appropriate initiators, such as water, glycerine, propylene glycol, etc. Particularly suitable are polyoxyalkylene diols or triols characterized by the formula:

$$In\ddagger(OCH_2CHR)_nOH\ddagger_m$$

wherein In is the polyol initiator, R is a $C_1$–$C_2$ alkyl group, $m$ is 2 or 3, and $n$ is the number of oxyalkylene units per polyol chain.

Although the necessary water insolubility is achieved with polyoxybutylene polyols having an average molecular weight as low as 500, with polyoxypropylene polyols the average molecular weight must be greater than about 1,000 to achieve the required degree of water insolubility. Since it has been found that higher molecular weight polyols may also improve the strength of the reconstituted tobacco foil, polyols having a molecular weight in the range from 1,500 to 5,000 are particularly desirable. Block or heteric copolymers of propylene oxide and 1,2-butylene oxide may also be used if they have the proper water insolubility and viscosity.

The amount of polyol necessary for satisfactory pretreatment of the tobacco depends particularly on such factors as the particle size and surface area of the tobacco. However, in general from 5 to 30 weight percent and preferably about 10 to 20 weight percent, tobacco basis, of the polyol is incorporated with the finely divided tobacco, preferably by spraying and dry mixing. Other means for obtaining a surface coating of the polyol on the tobacco particles can also be used including treatment with a solution of the polyol in a volatile solvent such as methanol. Conventional tobacco additives, such as combustion aids or retardants can also be incorporated with the polyol-treated tobacco before blending with the binder.

As a further modification of the present invention, it has been discovered that addition of a small amount of a suitable antioxidant with the polyol used to pretreat the tobacco prior to mixing with the binder, results in enhanced color stability during the processing and drying of the resulting tobacco foil. The improved stability is particularly advantageous in permitting more rapid drying and higher drying temperatures without detrimental discoloration.

In practice the sterically hindered phenolic antioxidants approved for food and drug use, such as butyl-

ated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), nordihydroguiairetic acid (NDGA) and phenyl salicylate (salol), are preferred. Other commercial primary antioxidants, such as Santinox R or N-lauryl-p-aminophenol, are also suitable. Such food stabilizers as ascorbic acid, gallic acid, citric acid and malic acid are not effective at a practical concentration level although they may be present as minor components of suitable antioxidant compositions. The effective antioxidants are also generally water-insoluble but soluble in the hydrophobic polyols used to pretreat the tobacco. Thus they are readily incorporated in the pretreated tobacco by addition with the desired polyoxyalkylene polyol.

The effectiveness of the antioxidant is influenced by the nature of the polyol. For example, less antioxidant is required when a polyoxybutylene diol is used rather than a similar molecular weight polyoxypropylene diol. However, in general, a suitable antioxidant must be effective at a concentration of from about 100 to 5,000 p.p.m. based on the weight of treated tobacco. Within these limits, the preferred antioxidant and optimum concentration for a particular system can be determined by routine tests.

It has still further been noted that if the aqueous process solutions are contaminated with copper, iron or other heavy metal ions which promote oxidative discoloration of the tobacco, a suitable chelating agent such as calcium disodium ethylenediaminetetraacetate, disodium ethylenediaminetetraacetate, or sodium hexametaphosphate may be used to obviate their effect.

The invention disclosed herein is particularly advantageously used in conjunction with the process described by Savage and Aldrich in United States patent application Ser. No. 361,221, filed on Apr. 20, 1964, for the manufacture of reconstituted tobacco foil using an alkali-soluble methyl cellulose as the binder. The process involves intermixing finely divided tobacco with an alkaline solution of alkali-soluble methyl cellulose and extruding the resulting slurry into an acid salt coagulant bath to form a continuous, self-supporting film. When dried, the resulting tobacco foil has enhanced moisture resistance and suitable tensile strength and dimensional stability for use as a binder in the preparation of cigars and similar tobacco products. However, the tobacco often is darkened by contact with the aqueous process solutions and the reconstituted foil usually does not have the appearance and particularly the light color desired for use as an outer cigar wrap. By pretreating the tobacco with a hydrophobic polyol, as described herein, and then intermixing with the alkaline methyl cellulose solution, an improved reconstituted tobacco foil is obtained having a color comparable to that of the original tobacco.

The invention is not limited to use with an alkali-soluble methyl cellulose binder. It can be used with other water-soluble binders, for example, carboxymethyl cellulose, hydroxyethyl cellulose, a water-soluble methyl cellulose as well as such natural products as alginates, pectins, and plant gums, to enhance the color stability of the tobacco. Pretreatment of the tobacco with a hydrophobic polyoxyalkylene polyol, as described herein, can also be advantageously employed when water-insoluble binders are used if discoloration from contact with water is encountered during processing.



The following examples are given to illustrate further the invention described herein. Unless otherwise specified, all parts and percentages are by weight. The polyoxyalkylene polyols used are commercial products prepared by the addition of alkylene oxide to a conventional initiator. For convenience, they are identified by a letter indicating the alkylene oxide (E—ethylene oxide; P—1,2-propylene oxide; B—1,2-butylene oxide) followed by a number designating the average molecular weight. The comparative evaluations of the tobacco color were made by an experienced observer.

*Example 1.—Stabilized reconstituted tobacco foil*

(A) To a solution of 90 parts of sodium hydroxide in 800 parts of water was added 53 parts of alkali-soluble methyl cellulose (7%—$OCH_3$) having a viscosity of 72 cps. as a 2% solution in 6% NaOH at 20° C., 4 parts of a liquid polyoxyethylene glycol (M.W. 200) and 4 parts of a solid polyoxyethylene glycol (M.W. 4,000). The mixture was stirred and cooled to about 0° C. Finally the caustic solution of methyl cellulose was filtered through a 150 mesh screen and deaired.

(B) About 15 parts of Diol B–1000, a liquid polyoxybutylene glycol having a viscosity of about 300 centistokes (cs.) at 25° C. was sprayed onto 159 parts of finely ground (200 mesh), light golden shade tobacco. The dry mixture was thoroughly blended by tumbling in a sealed container to coat the tobacco particles with the glycol. Finally an aqueous tobacco slurry was made by adding 610 parts of water.

This tobacco slurry was slowly added and intermixed with the alkaline methyl cellulose solution (A). The slurry was deaired by brief centrifuging and then transferred to the reservoir of a film casting die having a 0.013" by 5" slit. By means of air pressure on the reservoir, the slurry was extruded beneath the surface of a $H_2SO_4$—$Na_2SO_4$ coagulating bath containing 16% sulfuric acid and saturated with sodium sulfate. The coagulated film was drawn through the bath with a contact time of about 30 seconds and then washed with hot water (60° C.), neutralized in a dilute sodium bicarbonate solution, rewashed with hot water and finally dried by contact with a heated steel roll having a surface temperature of about 120° C.

The dried reconstituted tobacco foil was golden brown in color, quite comparable to that of the initial tobacco and greatly superior to the unattractive dark brown color of a control foil prepared in the same manner without pretreatment of the tobacco with the Diol B–1000. It contained 0.8% acid calculated as sulfuric acid but no residual inorganic sulfate. It had a thickness of about 3 mils and was flexible and self-supporting over a wide range of temperature and relative humidity. The tobacco foil did not darken when a drop of water was left on its surface for several minutes.

(C) The effect of drying conditions on the color of the reconstituted tobacco film is illustrated in Table 1 with typical results from drying samples of the washed film described in 1B under several conditions. In general the best color is obtained by slow drying at ambient temperature. At temperatures above 40–50° C. darkening frequently occurs. However, if the foil has sufficient stability to be dried rapidly at temperatures of about 110–120° C., discoloration can be minimized.

TABLE 1.—DRYING CONDITIONS

| Method | Temperature, °C. | Time | Foil Color |
|---|---|---|---|
| Air dried | 25 | 8–12 hrs | Best, light golden. |
| Roll dried | 120 | 2–3 min | Excellent, light golden. |
| Do | 95–100 | 5–7 min | Discolored, brown. |
| Do | <90 | 10–15 min | Dark brown. |

*Example 2.—Polyoxyalkylene polyols*

Following the general procedure of Example 1, reconstituted tobacco foils were prepared using alkali-soluble methyl cellulose as a binder for tobacco pretreated with various polyoxyalkylene polyols. The polyols were applied to the tobacco as a liquid spray, or in the case of the solid Diol E–4000 as a melt or as a solution with liquid Diol E–200. About 10–20 wt. percent of each polyol was used based on the weight of tobacco. After coagulation and washing the tobacco foils were dried on a heated roll. The appearance and color of the foils were noted and samples taken for analysis and determination of physical properties.

From observations such as given in Table 2 it is evident that pretreatment with the hydrophobic polyols enhances the color stability of the tobacco during the processing. In general superior results were obtained with the butylene oxide derived polyols. A definite increase in tensile strength was noted with the B–2000 foil. Triols gave results generally similar to the corresponding diol of about the same molecular weight. The foils prepared from tobacco pretreated with water-soluble Diol P–400 and the E–polyols were noticeably discolored even before drying.

TABLE 2.—PRETREATMENT WITH POLYOXYALKYLENE POLYOLS

| Polyol | Water Sol., Wt. Percent 25° C. | Viscosity, cs., 25° C. | Observations of the Drying Tobacco Foil |
|---|---|---|---|
| Diol B–500 | <0.1 | 124 | Excellent color, stable at 120–125° C. |
| Diol B–1000 | <0.1 | 231 | Do. |
| Diol B–2000 | <0.1 | 558 | Best color, stable at 120–125° C. |
| Diol P–1200 | ~2 | 160 | Good color, darkens slowly at 120° C. |
| Diol P–4000 | <0.1 | 1,114 | Good color, darkens slowly at 120° C., brittle. |
| Triol P–1030 | <0.1 | 218 | Good color, darkens slowly at 120° C. |
| Diol P–400 | ∞ | 70 | Poor color, darkens at 100–120° C. |
| Diol E–400 | ∞ | 90 | Very poor color, darkens at 100–120° C |
| Diol E–4000 | ∞ | Solid | Poor color, darkens at 100–120° C. |

*Example 3.—Antioxidants*

As a screening test for antioxidants to be used with the hydrophobic polyols in the pretreatment of tobacco, a mixture of 10–20 parts of polyol and 1 part of antioxidant was thoroughly intermixed with 100 parts of finely divided tobacco. For the initial test Diol P–1200 was generally used as the polyol. This treated tobacco was then slurried with an alkaline solution containing about 30–40 parts of alkali-soluble methyl cellulose such as described in Example 1A. From each test slurry a thin film was cast or extruded, coagulated in a $H_2SO_4$—$Na_2SO_4$ bath, washed and dried. The effectiveness of the antioxidants was judged by comparison of these test foils with control films prepared without an antioxidant.

Typical results from this antioxidant test are given in Table 3. The sterically hindered phenolic antioxidants gave a marked improvement in tobacco color retention when the foil was dried at an elevated temperature of up to 120° C. while citric acid, malic acid, gallic acid, dextrose and propyl gallate were ineffective. Also illustrated in Table 3 is the influence of the polyol structure.

TABLE 3.—ANTIOXIDANT TEST

| | Polyol | Antioxidant | Observation of the Drying Tobacco Foil |
|---|---|---|---|
| A | Diol P–1200 | Phenyl salicylate | Excellent color and stability at 120° C. |
| | do | NDGA | Do. |
| | do | BHA | Do. |
| | do | N-lauroyl-p-aminophenol | Good; improved color stability at 120° C. |
| | do | p-Benzyloxyphenol | Do. |
| | do | Malic acid | Poor; darkens at 100–120° C. |
| | do | Citric acid | Do. |
| | do | Propyl gallate | Do. |
| B | Diol B–1000 | Phenyl salicylate | Excellent color and stability at 120° C. |
| | Diol B–2000 | do | Superior color and stability at 120° C. |
| | Diol P–4000 | do | Excellent color and stability at 120° C. |
| | Diol E–200 | do | Very poor. |

*Example 4.—Water-soluble binders*

The effect of the hydrophobic polyol pretreatment with several different commercial water-soluble cellulosic binders is shown in Table 4. A standard finely divided shade tobacco was used with appropriate pretreatment with 2.5 parts of polyoxyalkylene diol and 1 part of salol per 30 parts of tobacco. To 1 part of the untreated control tobacco or the pretreated tobacco was added 10 parts of a 4% aqueous solution of water-soluble methyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, or mixed cellulose ether. The test tobacco film was formed by casting the aqueous slurry on a glass plate and drying at about 93° C. While the test conditions were not optimum for each binder, the results show enhanced stability of the foils prepared from pretreated tobacco.

TABLE 4.—WATER-SOLUBLE BINDERS

| Binder [1] | Color Rating of Dried Tobacco Foils | | | | |
|---|---|---|---|---|---|
| | Control | B–2000 | B–2000+AO | P–4000 | P–4000+AO |
| Methocel MC, 50 cps | Poor | Fair-good | Good | Fair | Fair. |
| Methocel 65 HG, 50 cps | Fair | Very good | Best | Good | Good. |
| Natrosol 250 HEC | Poor | Fair-good | Fair | Fair-good | Fair. |
| Cellosize WP40 | do | do | do | Fair | Poor. |
| CMC, 72 cps | do | do | do | do | Do. |

[1] Methocel MC—A methyl cellulose containing from 27.5–31.5%—$OCH_3$ The Dow Chemical Company.
Methocel 65 HG—A mixed cellulose ether containing 27–29%—$OCH_3$ and 4–7.5% hydroxypropyl ether; The Dow Chemical Company.
Natrosol 250 HEC—A hydroxyethyl cellulose (M.S.=2.5) having a 1% aqueous viscosity of 1,500–2,500 cps. at 25° C.; Hercules Powder Company, Inc.
Cellosize WP40—A hydroxyethyl cellulose (M.S.=1.6) having a 2% aqueous viscosity of 75–125 cps.; Union Carbide Corporation.
CMC—Sodium carboxymethyl cellulose (D.S.~0.7); Hercules Powder Company, Inc.

*Example 5.—Organic-soluble binders*

Using the test tobacco mixtures described in Example 4, test foils were prepared using a 4% solution of organic-soluble methyl cellulose (42.5% —$OCH_3$) in 70 parts benzene-30 parts methanol. The test foils cast and dried at room temperature were evaluated for color and then a stripe of water was run across the film followed by re-drying. As shown in Table 5, the color stability of the initial solvent cast foils is very good even with the untreated tobacco. However, when the cast foils were exposed to water and redried, the improvement in color stability of the hydrophobic polyol treated foils was evident.

TABLE 5.—ORGANIC-SOLUBLE BINDER

| Tobacco Foil | Dried at ° C. | Color Rating of Tobacco Foils | | | | |
|---|---|---|---|---|---|---|
| | | Control | B-2000 | B-2000+AO | P-4000 | P-4000+AO |
| Solvent cast | 25 | Very good | Very good | Very good | Excellent | Excellent. |
| Water-striped | 25 | Poor | do | Fair | Fair | Poor. |
| Do | 100 | do | Fair | Fair-good | do | Fair-poor. |

We claim:

1. In a process for the preparation of a reconstituted tobacco foil from finely divided tobacco and a cellulosic binder wherein the tobacco and cellulosic binder are intermixed in the presence of water, the improvement whereby the tobacco has enhanced color stability during manufacture of the reconstituted tobacco foil which comprises:
   (A) Treating 100 parts of finely divided tobacco with from about 2 to 30 parts of a liquid polyoxyalkylene polyol wherein the oxyalkylene groups are oxypropylene and/or oxybutylene groups and characterized by:
      (1) a water solubility of less than about 2 weight percent at 25° C.,
      (2) a viscosity of 100 to 1,200 centistokes at 25° C., and
      (3) an average molecular weight of from about 500 to 5,000; and
   (B) Intermixing therewith the cellulosic binder and forming a reconstituted tobacco foil.

2. The process of claim 1 wherein the binder is an alkali-soluble methyl cellulose having a degree of substitution from 0.2 to 0.7.

3. The process of claim 1 wherein the binder is a water-soluble methyl cellulose.

4. The process of claim 1 wherein the binder is a water-soluble hydroxyethyl cellulose.

5. The process of claim 1 wherein the binder is a water-soluble carboxymethyl cellulose.

6. The process of claim 1 wherein the polyol is a polyoxybutylene diol.

7. The process of claim 1 wherein the polyol is a polyoxypropylene diol having an average molecular weight in the range from 1,000 to 5,000.

8. The process of claim 1 wherein from about 100 to 5,000 p.p.m. of a sterically hindered phenolic antioxidant is incorporated with the polyol and tobacco prior to intermixing with the binder.

9. The process of claim 8 wherein the binder is an alkali-soluble methyl cellulose having a degree of substitution from 0.2 to 0.7.

10. A reconstituted tobacco foil having enhanced color stability which comprises finely divided tobacco intermixed with from about 2 to 30 weight percent tobacco basis of a liquid polyoxyalkylene polyol wherein the oxyalkylene groups are oxypropylene and/or oxybutylene groups and characterized by:
   (1) a water solubility of less than about 2 weight percent at 25° C.,
   (2) a viscosity of 100 to 1,200 centistokes at 25° C., and
   (3) an average molecular weight of from about 500 to 5,000; and

a cellulosic binder and then formed into a reconstituted tobacco foil.

11. The reconstituted tobacco foil of claim 10 wherein the binder is an alkali-soluble methyl cellulose having a degree of substitution from 0.2 to 0.7.

12. The reconstituted tobacco foil of claim 10 wherein from about 100 to 5,000 p.p.m. of a sterically hindered phenolic antioxidant is incorporated with the polyol and tobacco prior to intermixing with the binder.

**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,893,400 | 7/1959 | Detert et al. | 131—15 |
| 2,927,588 | 3/1960 | Detert et al. | 131—15 |
| 2,971,517 | 2/1961 | Pihl | 131—15 |

**References Cited by the Applicant**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,797,689 | 7/1957 | Frankenburg. |

OTHER REFERENCES

W. O. Lundberg: "Autoxidation and Antioxidants," vol. II., Interscience, New York, 1962, Ch. 11.

E. Ott et al.: "High Polymers, vol V., Cellulose and Cellulose Derivatives," 2nd ed., New York, 1954, part II, Ch. IX.

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