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2,797,689

TOBACCO PRODUCTS AND PROCESS THEREFOR

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This invention relates to tobacco products adapted for smoking, and more particularly to smoking products in which a water-insoluble cellulose derivative is used in conjunction with tobacco.

This application is a continuation-in-part of my copending application, Serial No. 105,660, filed July 19, 1949, now matured as U. S. Patent 2,706,695 issued April 19, 1955. The aforesaid application discloses and claims coherent masses of comminuted tobacco in which the tobacco particles are held together by a water-soluble derivative of cellulose having dispersed therein a finely divided non-water-swelling siliceous catalyst. Tobacco sheets, filaments, shreds and the like, made from powdered tobacco and a water-soluble cellulose derivative, preferably a cellulose ether such as methyl cellulose or carboxymethyl cellulose, when utilized in cigarettes, cigars or other smoking products, were found by some smokers with unusually keen taste for or sensory response to tobacco smoke, to give off during smoking a trace of foreign material which was variously reported as being "woody," aldehydic or acidic. The addition of the powdered siliceous catalyst to the cellulose derivative used as the binding agent in such tobacco products was found to eliminate the foreign material in the smoke so that even discriminating smokers no longer had any adverse criticism of such products.

Tobacco products in the form of sheets, filaments and shreds have also been prepared from powdered tobacco and water-insoluble cellulose derivatives. Thus, it has been proposed that cellulose acetate be dissolved in a volatile organic solvent such as alcohol or acetone and this solution be applied to comminuted tobacco so that the particles adhere to one another. The organic solvent is removed by evaporation, preferably at a moderately raised temperature and at a subatmospheric pressure. Other water-insoluble cellulose derivatives like ethyl cellulose may similarly be used as a binding agent for tobacco particles by dissolving the cellulose derivative in a volatile organic solvent which is removed after the tobacco product has been formed. On the other hand, the water-insoluble cellulose derivative may be applied to the comminuted tobacco in the form of a water emulsion. In such case, the water along with any volatile emulsifying agent in the emulsion is removed by evaporation after the tobacco product has been formed. Still another type of water-insoluble cellulose derivative used in making coherent tobacco masses from powdered tobacco is illustrated by carboxymethyl cellulose and carboxymethyl hydroxyethyl cellulose. It is known that the salts, particularly the alkali metal and ammonium salts, of the acid derivatives of cellulose are soluble in water, but when aqueous solutions of these salts are neutralized with an acid such as sulfuric or hydrochloric acid, the acid derivatives of cellulose are converted into an insoluble gelatinous flock. However, the gelatinous material, after water washing, may be passed through a homogenizer or colloid mill to yield a uniform dispersion or suspension in water. Such dispersion of an acid derivative of cellulose may be applied to powdered tobacco to form sheets, filaments and shreds. After formation of the desired tobacco product, the water is eliminated by evaporation.

In all instances in which a water-insoluble cellulose derivative is used as a binding agent in a tobacco product,

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the smoke evolved from such a tobacco product is found objectionable by smoking connoisseurs who detect the presence of foreign material of a "woody," aldehydic or acidic nature in the smoke.

A principal object of this invention is to provide smoking products comprising tobacco and water-insoluble cellulose binders which are substantially free of the undesirable smoke components derived from the burning of the cellulose binders.

In accordance with this invention, a smoking product in which tobacco is present in conjunction with a water-insoluble cellulose derivative has incorporated therein a finely divided, siliceous, mineral-type material which being incombustible remains substantially unchanged throughout the burning process and functions like a catalyst in modifying the combustion of the cellulose derivative so that the resultant combustion gases and vapors are substantially free of the undesirable components formed when the cellulose derivative is burned in the absence of the siliceous material.

The finely divided, siliceous, mineral-type material has the property of modifying the combustion of the water-insoluble cellulose derivative so that a smoker can no longer detect the acidic or other undesirable smoke components developed in the ordinary combustion of the cellulose derivative. Typical suitable siliceous materials are acid-treated clays, heat-treated montmorillonite, and natural and synthetic silicates containing some hydrogen atoms which are relatively mobile. Inasmuch as these siliceous materials are not combustible and yet exert a favorable influence on the burning of water-insoluble cellulose derivatives, I believe that they act as catalysts in the sense that the usual aldehydic or acidic or hydrocarbon-type products of combustion are not at all formed or, if formed, are promptly further oxidized to the harmless form of carbon dioxide and water vapor so that the smoker observes no foreign taste or odor. For want of a better term, suitable siliceous materials will hereinafter be referred to as siliceous catalysts.

The siliceous catalysts of this invention are not to be confused with the typical combustion catalysts that have been suggested hitherto for use in tobacco products. Strangely enough, such combustion catalysts like the finely dispersed oxides of iron, copper or other heavy metals or alkali metal salts are worthless in overcoming the undesirable smoke components formed when a water-insoluble cellulose derivative is burned. On the other hand, it appears that a siliceous catalyst which is good for cracking hydrocarbons is good for avoiding the development of objectionable smoke components in smoking tobacco products containing cellulose derivatives. In short, siliceous catalysts known to be successful cracking catalysts of the petroleum refining industry are beneficial to tobacco smoking products containing a cellulose derivative. This surprising discovery may indicate that the pyrogenic decomposition products of the water-insoluble cellulose derivatives are similar, or identical with, hydrocarbons and that the function of the siliceous catalyst consists in cracking these hydrocarbons into smaller molecular units which are then readily and completely oxidized to carbon dioxide and water vapor.

It is today generally accepted that a certain "acidic" nature is essential for the effectiveness of catalysts for cracking high molecular hydrocarbons to lower molecular fragments. This property also seems to be a prerequisite for the efficiency of the siliceous catalysts used pursuant to my invention for the improvement of odors developed in igniting cellulose derivatives, such as ethyl cellulose or carboxymethyl cellulose. A class of catalysts with the proper acidic nature which can be used is that of solid particles containing silica and such amounts of difficultly reducible metal oxides that the molecular ratio of silica

to the other oxides exceeds appreciably the value of 1. As all these combinations of silica with other oxides, such as for instance, alumina, zirconia, titania, chromium oxide, magnesium oxide and others, contain small amounts of water, it is quite likely that the solid phase comprises a kind of complex acid in which some hydrogen atoms are in a rather mobile state especially at the surface of the solid particles. This view and experimental support for it have been presented by R. C. Hansford in a paper entitled, "A mechanism of catalytic cracking," *Ind. and Eng. Chem.*, 39, 849 (1947). The specific catalyst mentioned in this paper was composed of approximately 12% alumina and 88% silica (on dry basis). In another paper entitled, "Montmorillonite cracking catalyst," *Ind. and Eng. Chem.*, 41, 1485 (1949), Alexander Grenall has demonstrated the presence of hydrogen ion in Filtrol clay catalysts.

Silica gels which have been impregnated, even with as little as 1% alumina, have been shown to be efficient cracking catalysts by Pitzer in "Advancing Fronts in Chemistry," vol. 1, page 33, 1945, Reinhold Publishing Corp. Another cracking catalyst has been described by O'Kelly et al. in *Ind. and Eng. Chem.*, 39, 154 (1947), as being prepared by the co-precipitation of the hydrous oxides of silicon and aluminum in a weight ratio of 9:1 of silica to alumina. A tricomponent cracking catalyst consisting of silica, alumina and zirconia has been described by Thomas et al. in *J. Am. Chem. Soc.*, 66, 1694 (1944).

Cracking catalysts can be prepared by using natural clays as a starting material. Many clays contain silica and alumina in a ratio which corresponds to the postulate that the number of moles of silica exceed appreciably the number of moles of alumina or other oxide. However, some of these clays contain, instead of mobile hydrogen atoms combined with excess silica, other atoms, such as alkali and alkaline earth atoms. Such clays can be "activated" by removing part or all of the alkali and alkaline earth atoms and replacing them with hydrogen atoms by treatment with acid. Other clays, which already in their original composition have a potential acidic nature by having the proper ratio of silica to alumina or other oxides, can be activated by heat treatment (cf. Alexander Grenall l. c.).

All of the aforementioned natural and synthetic cracking catalysts are effective siliceous catalysts for the purpose of this invention. To recapitulate, my siliceous catalyst is a combination of a major weight proportion of silica and a minor weight proportion of one or more difficultly reducible metal oxides; this combination may be effected synthetically or it may be derived from natural materials like clays through activation by heat and/or acid treatment.

The siliceous catalysts of this invention are not to be confused with ordinary or unactivated natural minerals, such as clay, kaolin, fuller's earth and bentonite, which have heretofore been proposed in tobacco products. For instance, U. S. Patent 2,592,553 to Frankenburg and Garbo discloses that bentonite added to a paste of tobacco powder in a viscous aqueous solution of methyl cellulose swells in water and tends to form a coherent inorganic skeleton or reinforcing network when the paste is converted into a dry tobacco sheet. In contrast thereto, the siliceous catalysts effective for the purpose of this invention are non-water-swelling and activated.

The siliceous catalyst is intimately and uniformly disposed in the water-insoluble cellulose derivative while it is in a fluid condition such as dissolved in an organic solvent or emulsified in water. The siliceous catalyst may be added to the cellulose binding agent before or after or simultaneously with the addition of comminuted tobacco. In any event, the catalyst particles are enveloped by the cellulose binding agent.

The quantity of siliceous catalyst required in the tobacco products of this invention depends upon the efficacy or activity of the chosen siliceous catalyst and the propensity

of the selected cellulose derivative to give off acidic or other undesired gases during combustion. In general, the addition of the siliceous catalyst falls in the approximate range of 20% to 60% based on the weight of cellulose derivative in the tobacco product. The preferred siliceous catalysts, like good hydrocarbon cracking catalysts, are usually employed in the proportions of about 45% to 55% based on the weight of cellulose derivative used in the tobacco product.

It is often advisable, where the product of this invention is made in sheet form and is later rolled or bent sharply as in making cigars, that the product contain a plasticizer to increase the flexibility and cracking resistance of the sheet. Additions of plasticizers such as glycerine and sorbitol of the order of 5% to 20% by weight, based on the weight of dry tobacco used, to tobacco sheets or filaments made with water-insoluble cellulose derivatives exert an appreciable plasticizing effect.

In an illustrative embodiment of the invention, a water solution containing 4% by weight of the sodium salt of carboxymethyl cellulose (high viscosity grade) is extruded in the form of strings or rods approximately $\frac{1}{16}$ inch in diameter into a bath of 20% hydrochloric acid. The volume of the acid bath is double that of the salt solution injected thereto. The extruded material remains in the acid bath approximately 15 minutes during which time the acid converts the sodium salt of carboxymethyl cellulose into insoluble, gelatinous carboxymethyl cellulose. The free-acid derivative of cellulose, thus prepared, is removed from the acid bath and washed for approximately one-half hour in a water bath at room temperature through which there is a continuous flow of water. The gelatinous carboxymethyl cellulose is removed from the water bath, drained and passed through a colloid mill to form a substantially homogeneous dispersion. The resulting dispersion contains approximately 2.5% by weight of carboxymethyl cellulose.

For each pound of the free-acid derivative of cellulose in the homogeneous dispersion, there is added one-half pound of powdered siliceous catalyst, having a particle size of less than 200-mesh. Specifically, the siliceous catalyst is a silica gel containing approximately 11% by weight of alumina (ground "Sovabead" catalyst of Socony-Vacuum Oil Company). Dry-ground tobacco passing through an 80-mesh screen is then mixed with the catalyst-containing aqueous dispersion of carboxymethyl cellulose in the proportion of 1 pound of tobacco to 5 pounds of the aqueous dispersion. Glycerine is added to the resulting tobacco paste in the proportion of 8 pounds of glycerine to each 100 pounds of dry tobacco in the paste.

The tobacco paste is spread as a layer about $\frac{1}{60}$ inch thick on a stainless steel conveyor belt by a reverse-roll coater. The stainless steel belt travels through a dryer wherein a flow of air at a temperature of approximately 120° F. dries the wet layer of tobacco paste to a coherent tobacco sheet. The finished tobacco sheet has a moisture content of about 20% by weight.

Comparative smoking tests performed with the tobacco sheet just described and another tobacco sheet identical thereto except that the siliceous catalyst is absent, show that the siliceous catalyst eliminates the acidic smoke components ordinarily produced in the burning of carboxymethyl cellulose. In short, the addition of the siliceous catalyst makes the tobacco sheet entirely acceptable to very discriminating smokers.

While the description of my invention has been presented hereinbefore largely in terms of the embodiment wherein comminuted tobacco is formed into coherent, continuous bodies like sheets with the aid of a water-insoluble derivative of cellulose, it is obvious that the advantages of my discovery of siliceous catalysts to modify beneficially the burning of water-insoluble cellulose derivatives are applicable to any other type of smoking tobacco product which contains such a cellulose derivative. To illustrate, cigarettes may be manufactured in which

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the conventional paper covering is replaced by a film made from a water-insoluble cellulose derivative. By incorporating a siliceous catalyst in the film prepared from a water-insoluble cellulose derivative, the novel cigarettes will burn satisfactorily without permitting the cellulose derivative to give off the usual irritating vapors and gases. If desired, a white pigment such as titanium dioxide or calcium carbonate may be added along with the siliceous catalyst to the cellulose derivative while it is in a fluid condition. The fluid mixture comprising the water-insoluble cellulose derivative, siliceous catalyst and white pigment is then cast and dried as a white film to resemble the white paper covering which it replaces in this new type of cigarette.

As a further illustration, tobacco leaves may be joined with one another by lapping the leaves along their edges and using a water-insoluble cellulose derivative as the binding agent between the overlapped tobacco leaves. In this way, it is possible to form a continuous sheet from individual tobacco leaves and the incorporation of a siliceous catalyst in this product will prevent the evolution of undesirable combustion gases from the cellulose derivative when cigars or like smoking products made from this type of sheet are burned in the course of smoking.

In general, tobacco sheets, filaments and shreds made of powdered tobacco and a water-insoluble cellulose binding agent are acceptable to smokers when the cellulose binding agent does not exceed 15% by weight, based on the weight of the tobacco in the smoking product, and the siliceous catalyst is at least 20% by weight, based on the weight of the cellulose binding agent. The binding agents contemplated in this invention fall into two categories of water-insoluble cellulose derivatives, i. e., neutral derivatives such as esters and ethers of cellulose as illustrated by cellulose acetate and ethyl cellulose, respectively, and free-acid derivatives as illustrated by carboxymethyl cellulose. While the water-solubility or -insolubility of any free-acid derivative of cellulose varies with many factors of its preparation, the neutral derivatives of cellulose are characteristically insoluble in water. The use of my siliceous catalyst with a free-acid derivative of cellulose is claimed in my copending application Serial No. 105,660 to the extent that such cellulose derivative is partially soluble in water.

As used in this specification and the appended claims, the term, water-insoluble cellulose derivative, means a cellulose derivative substantially free of nitrogen, sulfur, phosphorus and the halogens; in short, derivatives giving undesirable products of combustion or of dry distillation should be avoided.

Those skilled in the art will visualize many other modifications and variations of the invention set forth hereinabove without departing from its spirit and scope. Accordingly, the claims should not be interpreted in any restrictive sense other than that imposed by the limitations recited within the claims.

What is claimed is:

1. In the manufacture of tobacco smoking products from tobacco and a water-insoluble cellulose derivative, used as a binding agent for said tobacco, the improvement of dispersing a finely divided non-water-swelling siliceous catalyst substantially uniformly in said cellulose derivative, while said cellulose derivative is in a fluid condition, to suppress the evolution of undesirable gases from said cellulose derivative during the smoking of said smoking products, said siliceous catalyst amounting to at least about 20% by weight of said cellulose derivative.

2. The process of claim 1 wherein said cellulose derivative in a fluid condition is gelatinous carboxymethyl cellulose uniformly dispersed in water.

3. The process of claim 1 wherein said siliceous catalyst is a hydrocarbon cracking catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide.

4. In tobacco smoking products, the improvement of a binding agent as a component of said smoking products comprising a water-insoluble cellulose derivative in film form and a finely divided non-water-swelling siliceous catalyst dispersed in and enveloped by said cellulose derivative to suppress the evolution of undesirable gases from said cellulose derivative during the smoking of said smoking products, said siliceous catalyst amounting to at least about 20% by weight of said cellulose derivative.

5. The tobacco smoking products of claim 4 wherein said cellulose derivative is a free-acid derivative of cellulose and said siliceous catalyst is a hydrocarbon cracking catalyst, synthetically prepared and consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide.

6. The tobacco smoking products of claim 4 wherein said cellulose derivative is carboxymethyl cellulose and said siliceous catalyst is a hydrocarbon cracking activated clay.

7. In tobacco smoking products wherein tobacco particles are held together by a water-insoluble cellulose derivative, the weight proportion of said cellulose derivative being minor to that of said tobacco particles, the improvement of a finely divided non-water-swelling siliceous catalyst dispersed in and enveloped by said cellulose derivative to suppress the evolution of undesirable gases from said cellulose derivative during the smoking of said smoking products, said siliceous catalyst amounting to at least about 20% by weight of said cellulose derivative.

8. The tobacco smoking products of claim 7 wherein said cellulose derivative is a free-acid derivative of cellulose and said siliceous catalyst is a hydrocarbon cracking catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide.

9. The tobacco smoking products of claim 7 wherein said cellulose derivative is carboxymethyl cellulose and said siliceous catalyst does not exceed about 60% by weight of said carboxymethyl cellulose.

10. The tobacco smoking products of claim 7 wherein said cellulose derivative is carboxymethyl hydroxyethyl cellulose and said siliceous catalyst does not exceed about 60% by weight of said carboxymethyl hydroxyethyl cellulose.

11. The tobacco smoking products of claim 7 wherein said cellulose derivative is a neutral derivative of cellulose and the said siliceous catalyst is a hydrocarbon cracking catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide.

12. The tobacco smoking products of claim 7 wherein said cellulose derivative is ethyl cellulose and said siliceous catalyst does not exceed about 60% by weight of said ethyl cellulose.

13. The tobacco smoking products of claim 7 wherein said cellulose derivative is cellulose acetate and said siliceous catalyst does not exceed about 60% by weight of said cellulose acetate.

14. A novel cigarette comprising a film of a water-insoluble cellulose derivative as the outer covering thereof and a finely divided non-water-swelling siliceous catalyst embedded in said film to suppress the evolution of undesirable gases from said film during the smoking of said cigarette.

15. The novel cigarette of claim 14 wherein said cellulose derivative is carboxymethyl cellulose.

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