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2,809,637

IMPROVED TOBACCO PRODUCTS AND CIGARETTE PAPER AND METHODS OF MAKING SAME

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This invention relates to methods of treating tobacco and improved tobacco compositions and appurtenances.

In my earlier patent U. S. 2,460,284 issued February 1, 1949 it was shown that when cured tobacco receives an additional treatment with solubilized chlorophyll, or its related compounds, the finished tobacco, in the process of smoking, undergoes a fuller oxidation by reason of a continuous supply of activated oxygen evolved directly from the chlorophyll distributed throughout the tobacco. In like manner my patent U. S. 2,460,285 issued February 1, 1949 discloses the fuller oxidation of cigarette paper when said paper carries a small portion of solubilized chlorophyll distributed therethrough.

To the accomplishment of ends above cited it was found most practical to spray tobacco, as well as its wrapper, with an alcoholic solution of chlorophyll, or with an aqueous solution of water-soluble chlorophyll, such as chlorophyllins, and allow the material to dry.

The procedure here described leads to a highly extended surface of chlorophyll, preferably in that of its most active form—water-solution chlorophyllin. In the presence of air, however, there is ever a tendency of the chlorophyll to undergo decomposition by way of autoxidation, especially in summer weather. Hence it has become necessary to seek some means of protecting chlorophyllin if there is to be any assurance of its readiness at all times to function as an oxidant.

In nature herself we have the answer. Here we find not alone a protectant to the porphyrin, chlorophyll, but also a protectant to this protectant. The first protectant, as well known, is made up of carotenoids, notably alpha, beta and gamma carotenes, which function both in speeding up the oxidizing action of chlorophyll and in repressing excessive oxygen from destroying chlorophyll. The second protectant is alpha tocopherol (vitamin E) which protects both chlorophyll and especially the carotenoids against their own oxidation. There are still other protectants, among the concomitants of chlorophyll in nature, not the least of which is vitamin K, especially protective against oxidation of unsaturated molecules even when it is present in less than one-millionth part. Both vitamin E and vitamin K are known structurally as quinoids.

Commercial chlorophyll is extracted directly from dried green leaves, chiefly alfalfa. Degradation of verdure through the action of an association of solvents leads to complete break-down of the chloroplasts that constitute the seat of oxidative-reductive activity resident in a living plant. In this break-down chlorophyll, its congeners and concomitants together with enzyme aggregates, are totally resolved into the individual components and separated chromatographically. Heretofore, no practical application of the entire oxidative-reductive unit existant in the stroma of chloroplast has been possible, simply for the reason that up to within a few years this truly physiological unit had not been isolatable as such.

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Fortunately, of late, the Berkman chlorophyll-unit as described in U. S. Patent 2,567,362 issued Sept. 11, 1951; has come into the market. This unit is composed of chlorophyll-a; chlorophyll-b; alpha, beta and gamma carotenes; lycopene; xanthophyll; alpha tocopherol (vitamin E); methyl phytyl naphthoquinone (vitamin K) and certain lipids, the last named serving chiefly as protective coating. The whole of this unit may be described as the physiological unit of plant life, and a complex pigment nuclei embedded in a phospholipid. In this context this physiological unit will be described as "chlorophyll-carotenoid-quinoid complex." This "complex" embraces generally the total composition of plant chloroplast exclusive of the cellulosic components and includes waxes, sterols and phospholipids. The phospholipids play no chemical role in the present invention but present or exert no deleterious effect. Hence more explicitly the term "chloroplastic complex" is to be understood as defining the entire unresolved catalyst and pigment within the stroma of chloroplasts of living plant cells.

Resolution of the chloroplastic complex into respective green chlorophyll and orange carotenoid fractions may readily be effected, but the original aggregate is most outstanding to all purposes. Primarily is this chloroplastic complex noted for its stability to light and heat and for its oxidative activity operative without danger to its own self-oxidation.

Closeness of composition between this physiological unit or chloroplastic complex, as now securable in the market, and the actual unit or complex as existant within the green leaf has been well demonstrated through chemical analysis; and studies carried out to compare the oxidizing effect of said chloroplastic complex over against that of just plain chlorophyll of commerce gave most interesting results as is illustrated by the following experiments.

Experiment 1

Into a three-necked flask, carrying 1 gram of sodium-copper chlorophyllin dissolved in 1000 cc. of distilled water at 30° C., and properly fitted with inlet and outlet tubes and thermometer, was passed a current of 10,000 cc. of carbon monoxide and 25,000 cc. of air at same temperature, and in the course of one hour. The resulting carbon dioxide, collected in lime water amounted to 2.10 grams (complete oxidation of 10 liters of carbon monoxide would have yielded 19.80 grams of the CO₂).

Experiment 2

Into the same flask, as in Experiment 1, there was admitted 1 gram of the physiological chlorophyll unit suspended in 1000 cc. of distilled water, at 30° C. and a current of 10,000 cc. of carbon monoxide and 25,000 cc. of air at the same temperature, passed through the flask in the course of one hour. The carbon dioxide collected from effluent gas weighed 4.56 grams. Complete oxidation of these 12.50 grams (10,000 cc.) of carbon monoxide would have yielded 19.8 grams of CO₂.

Hence the oxidation of carbon monoxide by chlorophyll, though slow enough at 30° C. is actually doubled (or is twice as effective) under the influence of the physiological chlorophyll unit. Difficult as it is in dealing with an insoluble agent the marked effectiveness here of the chloroplastic complex is clearly demonstrated. So great is the effectiveness of this chloroplastic complex, and other analogous porphyrin-carotenoid-quinoid complexes, that even when adsorbed chromatographically upon an adsorbent, it can be shown that its effect upon passing vapors is in no way repressed. Rather, it is increased. Certain toxic vapors such as carbon monoxide and aldehydic vapors from burning tobacco were proved to be greatly reduced by an adsorbed chloroplastic com-

plex; and this is in the face of the fact that the adsorbent which carried the chloroplastic complex did not carry it homogeneously distributed.

It is known that precipitated calcium carbonate, as well also as other inert earth metal oxides, hydroxides and carbonates, may serve to adsorb this active chloroplastic complex and the latter may be abundantly capable of oxidizing the vapors that pass near and over said adsorbent. Most noteworthy, however, is the protection against heat afforded this chloroplastic complex by the refractory nature of adsorbent itself. Thus, there is established a novel procedure for contacting, for example, tobacco and its wrappers with an oxidative catalyst, not highly diminished and dispersed through the actually combustible cellulosic or other organic media, but one that is encased within a shield resistant to conflagration up to the point where interior of shield reaches the temperature of decomposition of catalyst.

It is here that cigarette paper offers an ideal locale for experimental observation. Some 20-45% of the weight of cigarette paper is made up of calcium carbonate to promote slow and even burning of paper and likewise to present a highly desirable whiteness to the paper itself. The weight of cigarette paper is approximately $\frac{1}{10}$ of the weight of total cigarette. In the earlier patent, above cited, the cigarette paper as such in the early pulp stage was sprayed with chlorophyll solution and the green-colored pulp finished by impregnation with calcium carbonate. The result is, of course, a green-colored cigarette paper. By employing this new procedure it is possible to introduce ordinary chlorophyll into the calcium carbonate or "filler" and in turn to introduce this filler into cigarette at time of finishing said paper. The result is still a green-colored cigarette, little more to be preferred over the procedure outlined in the earlier patent.

When the physiological chlorophyll unit, i. e., the chloroplastic complex, or a chemically similar unit of porphyrin-carotenoid-quinoid type, is made to enter this picture, an entirely new panorama is presented. This insoluble chloroplastic complex cannot be applied as a spray. It can, however, be triturated with calcium carbonate; and as an adsorbent this calcium carbonate (as well also as other earth metal bases) withdraws to itself more deeply the green chlorophyll and next following the orange carotenoids, with the result that the triturate of calcium carbonate with chloroplastic complex is of the faintest yellow if there is only so much as 20 times as much base as organic complex. In the finished cigarette paper the concentration of the chloroplastic complex in the weight of calcium carbonate used will scarcely exceed 1 part in 200. Hence the color of finished cigarette paper will differ only slightly (on the yellowish gray side) from the generally accepted white paper.

This invention, therefore, comprehends the employment of chlorophyll-carotenoid-quinoid lipidized calcium carbonate, or other white insoluble oxides or carbonates herein suited, intermingled with cigarette paper at the end of the pulp stage in manufacture. The percentage of chloroplastic complex in total weight of paper, on dry basis, may vary between the limits of approximately $\frac{1}{100}$ of 1% to not in excess of 2% for the attainment of ends here desired, namely, a fuller oxidation of the more volatile aldehydic vapors as well also as oxidation of greater portion of carbon monoxide issuing from the cigarette both in primary smoke (entering the mouth) and in secondary smoke (escaping directly from the lighted cigarette).

This invention comprehends further the employment of cigarette paper so impregnated with chlorophyll-carotenoid-quinoid-lipidized calcium carbonate in the wrapping for shredded tobacco likewise impregnated with similar percentage of chlorophyll-carotenoid-quinoid-lipidized calcium carbonate or with the usual form of shredded tobacco not so impregnated.

The marketable advantage of this invention resides in

the blanking out of the somewhat undesirable green tinge in color of cigarette paper that has been treated with generally procurable water-soluble chlorophyll or even with solubilized chlorophyll as cited in my above mentioned patents.

The practical advantage of this invention resides in the graded diffusion of various components of the chloroplastic complex within the calcium carbonate particles such that the green or chlorophyllic portion becomes more deeply adsorbed whereas the orange or carotenoid portion left on the surface of said particles constitutes the more heat-resistant portion and serves to protect longer the interior portion, yet both at all times functioning together synergistically as oxidants for toxic vapors that pass near or over the particles.

The characterizing feature of this invention resides in the depositing of an insoluble active oxidant within the interstices of an inorganic refractory adsorbent thereby to increase protection of the entire oxidant against light and heat, as contrasted with same oxidant contained within the interstices of an easily charable and decomposable organic medium as is tobacco and its wrapper, and as set forth in my above mentioned patents. The composite oxidant here is far more effective than ordinary chlorophyll be it highly dispersed throughout the organic medium or actually carried in the "filler." At all events this invention presents a means of materially prolonging the oxidizing action of chlorophyll.

The method of procedure in carrying out this invention comprehends simply a trituration of desired quantity of chloroplastic complex with the given quantity of precipitated calcium carbonate, or similar white base; the latter generally, does not exceed 20 to 25% of the weight of dry cigarette paper pulp. On the basis of 75 grams of cigarette paper pulp (dry basis), 25 grams of precipitated calcium carbonate will be triturated thoroughly with 0.1 gram of chloroplastic complex (in fine powder), and the pulp and filler well intermingled; hereby, the total weight of finished paper will carry $\frac{1}{10}$ of 1% oxidant.

Another method of applying the triturate of precipitated chalk and chloroplastic complex comprises dusting the cigarette paper with the triturate just prior to passing the paper through the final finishing rolls. However, the distribution or interspersing of the triturate is not as well assured by this procedure.

In the case of shredded tobacco a much smaller proportion of calcium carbonate is called for; hence approximately this same percentage of chloroplastic complex will need be triturated with only a few grams of calcium carbonate and the triturate thoroughly rubbed into the tobacco.

Another practical procedure, somewhat saving in cost, contributory to involvement of the maximum number of calcium carbonate particles, consists in triturating green leaves directly with calcium carbonate or other white inert adsorbent. If the leaves have lost too much of their water content a trace of water or other solvent may be added, whereupon it will be found that the active chloroplastic complex will largely have been adsorbed by the calcium carbonate and this light yellow-colored triturate can be employed exactly as in previous instances. The quantity of such triturate to be used in any specific case can only be determined by a chemical analysis of said triturate once it is prepared.

A point of distinction between the present invention and my previous invention lies in the state of insolubility of the chlorophyll and in the intimate contact of the organic medium with each factor of the complex, exactly as present in the green leaf. In line with earlier patent it is perfectly possible to introduce in an inert adsorbent a solubilized chlorophyllin, followed with any one or more of the carotenoid class; this association, however, lends only a modicum of protection to the chlorophyllin, as when once separated from its congeners and concomitants, it never again is capable of resisting for any

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length of time the destructive action of oxygen and heat. Thus, too, solubilized chlorophyllin does not surrender its bleeding out properties as when paper so treated comes in contact with the mouth.

I claim:

1. A method of enhancing the smoking quality of cigarettes which comprises impregnating the paper wrapper thereof with an insoluble earth metal hydroxide or carbonate adsorbent carrying a water-insoluble chloroplastic complex as directly securable from chloroplasts of green leaves, the quantity of said complex not exceeding substantially 2% of the dry weight of the cigarette wrapper.

2. A method of enhancing the smoking quality of cigarettes which comprises impregnating the paper wrapper thereof with precipitated calcium carbonate previously triturated with a water-insoluble chloroplastic complex as directly derived from green leaves, the quantity of said complex comprising between approximately $\frac{1}{100}$ of 1% to about 2% of the weight of the paper.

3. An article of manufacture including a triturate comprising an inert refractory inorganic adsorbent and a water-insoluble chloroplastic complex derived from green leaves, and an organic medium chosen from the group consisting of cellulose and tobacco, said triturate being interspersed with said organic medium to facilitate the combustive oxidation of the latter and its decomposition products.

4. An article of manufacture comprising a triturate including an inert refractory organic adsorbent and a water-insoluble chloroplastic complex derived directly from green leaves, and an organic medium interspersed with said triturate, said organic medium being chosen from the group consisting of purified cellulose and tobacco, whereby said organic medium will undergo speedier and more complete combustive oxidation due to the presence of said complex.

5. A method of effecting fuller oxidation of an organic medium, chosen from the group consisting of purified cellulose and tobacco, in the presence of air, comprising the step of interspersing in said organic medium of a triturate of a refractory inorganic adsorbent with a water-insoluble chloroplastic complex.

6. A cigarette comprising shredded tobacco and a paper

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wrapper, means interspersed throughout said tobacco and wrapper to effect fuller oxidation thereof, said means including an inert inorganic adsorbent and a water-insoluble chloroplastic complex adsorbed within said adsorbent, the quantity of said complex per se not exceeding substantially 2% of the dry weight of the cigarette.

7. A cigarette paper including 10% to 25% of its weight of an adsorbent selected from the group comprising insoluble earth metal hydroxides and insoluble earth metal carbonates, and a water-insoluble chloroplastic complex directly derived from green leaves; said complex being carried by said adsorbent and said complex being present in an amount not exceeding substantially 2% of the dry weight of the paper.

8. As an article of manufacture, thin cellulosic sheets adapted for use as cigarette paper comprising an adsorbent selected from the group comprising insoluble earth metal hydroxides, and insoluble earth metal carbonates having incorporated therewith as a triturate a chloroplastic complex derived directly from green leaves, said complex being present in an amount not more than substantially 2% of the dry weight of the paper.

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