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TOBACCO PRODUCT

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This invention relates to novel combinations of plasticizers with water insoluble adhesives in tobacco products to impart new and useful properties.

Tobacco sheets composed of finely divided tobacco imbedded in an adhesive with flavoring agents and other additives are well known in the commercial production of smoking articles. For example, such sheets can be used to replace tobacco leaf as cigar binder on standard machines, or they can be shredded to form cigarette fillers. These applications do not require great pliability or extensibilty of the sheets, and water soluble gums may be employed as adhesives in either case because the tobacco sheet material does not come in direct contact with the mouth of the smoker.

In order to overcome some of the drawbacks of water soluble gums, where wet strength is desirable, it has been proposed to employ water insoluble adhesives dissolved in organic solvents to form tobacco sheets. Such adhesives include water insoluble esters and ethers of cellulose, amylose and other carbohydrate materials which are non-toxic and have acceptable odors in the products of combustion. The wet tensile strengths of such sheets are generally very good without addition of any fibers. However, the pliability and particularly the elongation is uniformly poor when the sheets contain a substantial amount of tobacco (50% or more of the sheet weight). For this reason little or no commerical use has been made of water insoluble adhesives in tobacco sheets, although such sheets have been known in the laboratory for many years. Efforts to plasticize tobacco sheets with many common types of plasticizers have been uniformly unsuccessful in imparting sufficient elongation to make them usable on cigar machines as wrappers for cigars.

This invention embodies, in essence, new combinations of tobacco, water insoluble adhesives and certain types of plasticizers of highly specific chemical structure, which can be formed into sheets useful as cigar wrappers and in other smoking articles. Such sheets have excellent elongation, pliability and tensile strength, either wet or dry, and can be used on standard cigar machines as a replacement for natural leaf cigar wrappers. The invention also relates to the manufacture and use of such sheets and of smoking articles containing them.

It is an object of the invention to provide plasticizers of highly specific chemical structure which will confer new and useful properties on tobacco sheets made with water insoluble adhesives.

A further object of the invention is to prepare sheets from tobacco, plasticizer and a water insoluble adhesive which contain a high proportion of tobacco and which also possess desirable physical properties such as elongation.

A further object of the invention is to manufacture cigar wrappers from tobacco powder, plasticizer and a water insoluble adhesive which can be applied continuously from a bobbin to cigars on standard cigar machines to produce a new type of cigar of good smoking quality and improved appearance.

A further object of the invention is to produce cigars, cigarettes, cigarillos and other smoking products of improved taste and appearance and greater ease of manufacture by incorporating therein synthetic tobacco sheet as wrapper, binder or filler.

The foregoing and other objects of this invention will be apparent from the following description.

The new and useful sheet forming combinations of this invention are characterized by a tobacco content of at least about 50% for the sake of taste, odor and appearance. The tobacco is finely ground and suspended in a solution of a water insoluble adhesive dissolved in an organic liquid solvent. A plasticizer of the type to be described is added, together with any dyes, flavoring agents, ash improvers, mold inhibitors or other inert ingredients which it is desired to incorporate into the finished tobacco sheet. Enough solvent is employed to form a thick slurry (generally 25–35% solids), which is extruded or cast to form a film of the desired thickness and sheet weight. The solvent is permitted to evaporate at ambient or slightly elevated temperatures, either at atmospheric pressure or under vacuum. Most economical operations require the recovery and recycle of the solvent by a solvent recovery unit.

Tobacco sheet may also be made by coating the tacky surface of a film of the non-tobacco ingredients or by coating of a layer of tobacco particles with the adhesive preparation.

Nearly all common plasticizers fail to produce tobacco sheet with sufficient elongation to be practical for use as cigar wrapper on a cigar machine under normal operating conditions. Such customary plasticizers include dioctyl phthalate, dibutyl sebacate, tricresyl phosphate, tributyl borate, di-isooctyl adipate, didecyl azelate, polyethylene glycols, polypropylene glycols, glycerol, glycerol esters, ethylene glycol monoethyl ethers and esters, diethylene glycol monoethyl ethers and esters and their isomers and homologues.

The first class of effective plasticizers of this invention consists of polyesters prepared by condensing a lower polyethylene glycol or glycerol with an aliphatic acid containing a straight chain of from six to ten carbon atoms. The term "lower polyethylene glycol" includes all of the reaction products of ethylene glycol and water with molecular weights below 250, specifically ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol and mixtures of any of these compounds.

The aliphatic dicarboxylic acids which react with these glycols to yield active polyester plasticizers, containing straight chains of six to ten carbon atoms, include adipic, pimelic, suberic, azelaic and sebacic acids, which may contain one or more small alkyl substituents on the six to ten membered chain of carbon atoms, or mixtures of any of these. In the practice of this invention the aliphatic dicarboxylic acid is condensed with less than twice the equivalent amount, but more than half the equivalent amount, of a lower polyethylene glycol by customary chemical methods of esterification to form the active polyester plasticizers of the invention. It is preferable to employ somewhat less than one molar equivalent of lower polyethylene glycol per mole of aliphatic dicarboxylic acid for best results.

The condensation can be carried out by any of the usual commercial or laboratory methods of esterification. One of the simplest procedures is to dissolve or suspend the reactants in benzene, add a few percent of concentrated sulfuric acid as catalyst, distill off the water formed in the reaction as an azeotrope with benzene and collect the water in a trap for azeotropic removal of water with provision for the benzene to reflux into the reaction vessel. When evolution of water ceases, generally after

four to eight hours at reflux temperature, the condensation is essentially complete. The polyester may conveniently be employed in the crude benzene solution after separation of the acid catalyst, or it may be further purified if desired.

Among the lower polyethylene glycols usable in this invention it is preferable to employ tetraethylene glycol. Polyesters derived from triethylene and lower glycols result in good elongation but reduce wet strength when incorporated into tobacco sheet, whereas polyesters produced from pentaethylene and higher glycols yield stiffer tobacco sheets with good wet strength but reduced pliability and extensibility. The best balance of properties is obtained with tetraethylene glycol in those applications which require both wet strength and good elongation, as in the case of tobacco sheet to be used for cigar wrapper. Modern cigar manufacturing machines require tobacco sheet with substantial elongation. Very satisfactory polyester plasticizers are produced from tetraethylene glycol combined with somewhat more than an equivalent amount of an aliphatic dicarboxylic acid containing, for example, a straight chain of from six to ten carbon atoms.

A particularly preferred embodiment of this invention is the use of polyesters prepared from tetraethylene glycol and a slight excess over the stoichiometric quantity of an aliphatic dicarboxylic acid containing a straight chain of eight carbon atoms. This chain may be unsubstituted as in the case of suberic acid, or it may contain one or more substituents of lower alkyl groups as in the case of 2-ethylsuberic acid. Although polyester plasticizers containing these acids impart the optimum physical properties to tobacco sheet, the acids are expensive and unavailable commercially in pure form. As a practical matter, therefore, these polyesters are generally synthesized from mixtures of cheap and commercially plentiful acids, and the composition of the acid mixture is adjusted to give an average chain length of close to eight carbon atoms. This results in some sacrifice of sheet quality, but the product is inexpensive and readily usable on standard cigar machines.

The second class of effective plasticizers of this invention consists of phenolic compounds or bisphenols which contain one or more substituents selected from the class consisting of hydroxymethyl, dialkylaminomethyl, cyclic aminomethyl or alkyl in positions ortho and para to the phenolic hydroxyl group. These phenolic compounds or bisphenols are produced by known methods from phenol, a bisphenol or a substituted phenol or bisphenol having not more than one substituent group in the positions ortho and para to the phenolic hydroxyl groups. The simplest method for introducing hydroxymethyl groups into the remaining unsubstituted ortho and para positions is to treat the starting phenol, bisphenol or substituted phenol with formaldehyde in the presence of sodium hydroxide by methods well known in the literature. The simplest method for introducing dialkylaminomethyl groups into the remaining unsubstituted ortho and para positions is to treat the starting phenol, bisphenol or substituted phenol with a mixture of stoichiometric quantities of formaldehyde and a dialkylamine. This synthesis is also well known in the literature as the "Mannich Reaction."

Either class of effective plasticizer of this invention, or mixtures of them, can be incorporated into tobacco sheet in the manner described above to produce the beneficial plasticizing effect necessary to make cigar wrapper which can be fed automatically from a bobbin to a cigar machine. Generally, flavoring and coloring materials, humectant and other inert ingredients such as ash improvers are incorporated into cigar wrapper sheet. Cigars prepared from tobacco sheet wrapper of this invention are light in color, smooth in texture, uniform in quality, inexpensive and do not dissolve or disintegrate in the mouth when wet with saliva. The same type of tobacco sheet, containing the plasticizers of this invention, may also be used as cigar binder or as a filler in other smoking articles such as cigarillos, little cigars, pipes or cigarettes. Some modification in sheet weight and in the proportions of the various ingredients employed may be necessary for the various applications mentioned. In each case, however, the essential feature is the use of tobacco sheet of this invention comprising at least about 50% tobacco by weight, a water insoluble adhesive cast or extruded in solution in an organic solvent and one or more of the plasticizers of this invention to which other ingredients may be added if desired.

The choice of the water insoluble adhesive to be employed in preparing the tobacco sheets of this invention is subject to certain limitations. The material must be nearly tasteless and completely non-toxic in the concentrations used, must possess good burn odor, must be virtually insoluble in water but soluble in whatever organic solvent is chosen for the process to form a viscous solution which can be cast or extruded, and for economic considerations should be inexpensive and readily available. These limitations practically indicate the choice of the ester or ether derivatives of carbohydrate high polymers such as cellulose, amylose and starches. Such materials, which are in widespread use, include cellulose esters, particularly cellulose acetate, the mixed esters such as cellulose acetate propionate and cellulose acetate butyrate and cellulose ethers such as methylcellulose and ethylcellulose. The molecular weight and degree of substitution of the cellulose or other carbohydrate derivative must be in the proper range to produce the solubility and viscosity characteristics mentioned above. Within these limitations the particular adhesive chosen will depend upon the specific flavor, burn odor and texture which the formulator wishes to impart to the finishing smoking article.

The solvent chosen for the manufacture of tobacco sheet of this invention must be one that will dissolve the adhesive, evaporates easily and is cheap and easily recoverable. High speed elevated temperature drying is desirable. Among the common solvents it is preferable to employ acetone, but methanol, ethanol, isopropyl alcohol, benzene, toluene, chloroform and methyl butynol or mixtures of any of these can be used with particular adhesives which dissolve in the solvent chosen.

This invention is more particularly described by the following examples.

Example 1

This example illustrates a preferred form of the invention.

A plasticizer solution was prepared from 365 grams of commercial adipic acid (2.5 moles), 282 grams of technical azelaic acid (1.5 moles) and 582 grams of tetraethylene glycol (3.0 moles) dissolved in approximately 2.5 liters of benzene. The reactants and solvent were placed in a five liter, five-neck, round bottom flask equipped with a motor stirrer, thermometer well, addition funnel, heating mantle, two reflux condensers and two modified Dean-Stark traps for collection of water. The solution was treated with 20 ml. of concentrated sulfuric acid as catalyst and refluxed with continuous stirring for 3.5 hours, after which time no more water was evolved. After cooling the benzene solution of crude polyester plasticizer was separated from the lower acid layer. The plasticizer content, determined by drying a sample to constant weight, was 37%.

This plasticizer was incorporated into tobacco sheet by the following procedure. Sixty grams of ball-milled, dry ground tobacco, all of which had passed through a 170-mesh screen, were suspended in a Waring Blendor in 350 ml. of acetone containing 30 grams of commercial cellulose acetate in solution. To this suspension was added 82 grams of the benzene solution, containing 30 grams of polyester plasticizer, to produce a solids content of about 27% by weight. The thick slurry was then cast into sheets with a casting knife clearance of

about 6 mils. The solvent was permitted to evaporate at room temperature and atmospheric pressure, and random samples of the sheets were removed for testing. The sheet tensile strength was over 330 grams per inch. After soaking in water for 45 seconds the tensile strength was still over 270 grams per inch (82% wet strength) and the elongation was between 35 and 40%.

Cigars prepared on a cigar machine with this tobacco sheet as wrapper were very satisfactory in taste and appearance.

Example 2

To illustrate the effect of changing the proportions of the reactants, three polyesters were prepared from varying amounts of tetraethylene glycol and technical azelaic acid by the procedure of Example 1. In the first case a 33% molar excess of tetraethylene glycol was employed; in the second case stoichiometric amounts of glycol and acid were charged; and in the third case the acid was present in 33% molar excess. The three polyesters were incorporated into tobacco sheets which were otherwise identical, composed of about 60% tobacco, 20% ethylcellulose (a commercial product described as having a medium ethoxy content and a viscosity of 100 cps. measured in solution under standard conditions) and 20% plasticizer. The solvent was acetone plus a small amount of benzene added with the plasticizer. The physical properties of the sheets, all cast with an 8-mil knife, appear in the following table:

Plasticizer	Sheet Properties		
	Wet Strength, Percent	Elongation, Dry, Percent	Elongation, Wet, Percent
1. (Excess glycol)	90	11	18
2. (Equimolar amounts)	88	22	24
3. (Excess acid)	75	25	32

It is evident from these data that an excess of dicarboxylic acid produces the best elongation in the sheet at the expense of a slight drop in wet strength.

Example 3

To illustrate the effect of varying the length of the straight chain of carbon atoms in the dicarboxylic acid employed for synthesis of the polyester plasticizers of this invention, seven plasticizers were prepared from tetraethylene glycol with different dicarboxylic acids by the procedure of Example 1. Each plasticizer was incorporated into tobacco sheet with the formulation of Example 2, and the physical properties of the resulting sheets were measured. The results appear in the following table:

Dicarboxylic Acid	Carbon Atoms	Wet Strength, Percent	Elongation, Dry, Percent	Elongation, Wet, Percent
Succinic	4	89	12	18
Glutaric	5	88	18	17
Adipic	6	84	21	23
Pimelic	7	82	30	35
Suberic	8	84	33	40
Azelaic	9	75	25	32
Sebacic	10	85	10	22

It is apparent that only the dicarboxylic acids having a straight chain of 6 to 10 carbon atoms produce tobacco sheets with sufficient elongation to be usable on cigar machines, and the optimum properties are observed when the chain length is about eight carbon atoms.

Example 4

To illustrate the effect of varying the polyethylene glycol, six polyester plasticizers were prepared by the procedure of Example 1 with technical azelaic acid and the following polyols: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol (average molecular weight about 400) and glycerol. In the case of glycerol only a stoichiometric amount of azelaic acid was employed for condensation. Each plasticizer was incorporated into tobacco sheet with the formulation of Example 2, and the physical properties of the resulting sheets were measured. The results appear in the following table:

Polyol	Wet Strength, Percent	Elongation, Dry, Percent	Elongation, Wet, Percent
Ethylene glycol	55	25	28
Diethylene glycol	56	23	27
Triethylene glycol	60	20	27
Tetraethylene glycol	75	25	32
Polyethylene glycol 400	90	10	13
Glycerol	53	25	24

Example 5

A plasticizer was prepared from 265 grams (1.36 moles) of tetraethylene glycol and 367 grams (1.82 moles) of a commercial mixture of isomeric ten-carbon dicarboxylic acids containing 2-ethylsuberic acid as the principal isomer, using the procedure of Example 1. A tobacco sheet was prepared from 15 grams (29%) of ethylcellulose (medium ethoxy—100 cps.), 7.5 grams (14%) of this polyester (in benzene solution) and 30 grams (57%) of tobacco suspended in 145 ml. of acetone. The sheet was cast with a six-mil knife and dried at room temperature. Tensile strength of the dry sheet was 320 grams per inch and tensile strength of the wet sheet was 227 grams per inch; elongation, 22% dry and 41% wet.

Cigars wrapped on a cigar machine with this sheet had good taste, color and appearance.

Example 6

To illustrate the use of adhesives derived from starch, tobacco sheet was prepared from 15 grams (26%) of amylose triacetate dissolved in 110 ml. of methyl butynol, 7.5 grams (13%) of the polyester plasticizer of Example 1, 5.0 grams (9%) of humectant (triethylene glycol) and 30 grams (52%) of tobacco with 0.3 gram of a commercial flavoring agent. The sheet strength was 407 grams per inch wet and 340 grams per inch dry (83% wet strength); elongation, 35% dry and 42% wet.

Cigars wrapped on a cigar machine with this sheet were light in color and had good taste and appearance.

Example 7

To illustrate the use of the second type of plasticizer of this invention, a tobacco sheet was prepared according to the formulation of Example 2 except that the plasticizer was technical 2,4,6,-tris-(dimethylaminomethyl) phenol. When cast with an 8-mil knife and allowed to air dry, the sheets weighed 3.9 grams per square foot; tensile strength, 312 grams per inch dry and 290 grams per inch wet; elongation, 40% dry and 37% wet.

This material made a satisfactory filler for cigarettes and also smoked well in a pipe.

Example 8

Into a one-liter Erlenmeyer flask were placed 18.8 grams of phenol (0.2 mole), 52.2 grams of morpholine (0.6 mole), 48.6 grams of a 37% aqueous solution of formaldehyde (.6 mole) and 100 ml. of methanol. The flask was shaken and cooled with running water for ten minutes until the evolution of heat had largely ceased. It was then allowed to stand at room temperature overnight, diluted with 500 ml. of water, and extracted four times with benzene. The benzene was stripped off under

reduced pressure to leave the crude Mannich base plasticizer, 2,4,6-tris-(morpholinomethyl) phenol.

A tobacco sheet was prepared with 15 grams (25%) of this plasticizer dissolved in 30 ml. of benzene, 15 grams (25%) of ethylcellulose (medium ethoxy—100 cps.) dissolved in 170 ml. of acetone and 30 grams of tobacco. A film of the non-tobacco material was formed and thereafter coated with tobacco dust. When the non-tobacco film was cast with a six-mil knife, the sheet tensile strength was 250 grams per inch dry and 200 grams per inch wet (80% wet strength); elongation, 29% dry and 50% wet.

Example 9

Three plasticizers were prepared from 4,4'-isopropylidenebisphenol and varying amounts of dimethylamine and formaldehyde by the procedure of Example 8. Plasticizer A was formed from equimolar quantities of the three reactants; plasticizer B had double this amount of amine and formaldehyde; and plasticizer C had four times as much of these reagents as plasticizer A. Each product was used as the plasticizer in a tobacco sheet of the formulation described in Example 8, and the physical properties of the sheets cast with a six-mil knife are listed in the following table:

Plasticizer	A	B	C
Sheet Weight, g./ft.^{2}	3.7	3.9	3.8
Tensile Strength, dry, g./in.	325	468	515
Tensile Strength, wet, g./in.	202	340	361
Elongation, dry, percent	45	45	45
Elongation, wet, percent	60	55	50

It is apparent that a higher degree of substitution on the aromatic nucleus results in increased tensile strength, both wet and dry, at little sacrifice in elongation.

Example 10

The reaction product of phenol and formaldehyde, 2,4,6-trimethylolphenol, is available commercially as a 70% solution in water or partially resinified material. A tobacco sheet was prepared with 7.5 grams (11.5%) of this technical product as a plasticizer, 15 grams (23%) of ethylcellulose (medium ethoxy—100 cps.), 42.5 grams (65.5%) of tobacco, 190 ml. of acetone and 35 ml, of benzene. When cast with an eight-mil knife, this sheet had a tensile strength of 468 grams per inch dry and 277 grams per inch wet; elongation, 16% dry and 36% wet.

This moistened sheet was wrapped on cigars on a cigar machine and after drying formed wrappers of excellent appearance, dark color and good taste.

There has thus been described a novel tobacco product made from finely divided tobacco, which constitutes at least half of the finished product by weight, a water insoluble adhesive and a novel plasticizer which may constitute up to one third by weight of the final product.

What is claimed is:

1. A composition of matter comprising in combination finely divided tobacco, a water insoluble adhesive and a material selected from the group consisting of polyesters, aminomethyl phenols and hydroxymethyl phenols.

2. As an article of manufacture a tobacco sheet comprising in combination finely divided tobacco, a water insoluble adhesive and a material selected from the group consisting of polyesters, aminomethyl phenols and hydroxymethyl phenols.

3. As an article of manufacture a cigar containing tobacco material made from finely divided tobacco, a water insoluble adhesive and a material selected from the group consisting of polyesters, aminomethyl phenols and hydroxymethyl phenols.

4. As an article of manufacture a cigarette containing tobacco material made from finely divided tobacco, a water insoluble adhesive and a material selected from the group consisting of polyesters, aminomethyl phenols and hydroxymethyl phenols.

5. A composition of matter comprising in combination finely divided tobacco, a water insoluble adhesive and a polyester plasticizer made from tetraethylene glycol and a material selected from the group consisting of azelaic acid, suberic acid, adipic acid, 2-ethyl suberic acid, pimelic acid and sebacic acid.

6. A composition according to claim 5 in which tetraethylene glycol is replaced at least in part by at least one material selected from the group consisting of glycerol, ethylene glycol, diethylene glycol and triethylene glycol.

7. A tobacco product comprising in combination a major part by weight of finely divided tobacco and a minor part by weight of a water insoluble polysaccharide adhesive derivative with up to one third by weight of a plasticizer selected from the class consisting of aminomethyl and hydroxymethyl substituted phenols, bis phenols and polymers of formaldehyde and phenols.

8. A cigar wrapper made from the composition of claim 1.

9. A cigar wrapper made from finely divided tobacco, cellulose acetate and a plasticizer prepared from tetraethylene glycol, adipic acid and azelaic acid.

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