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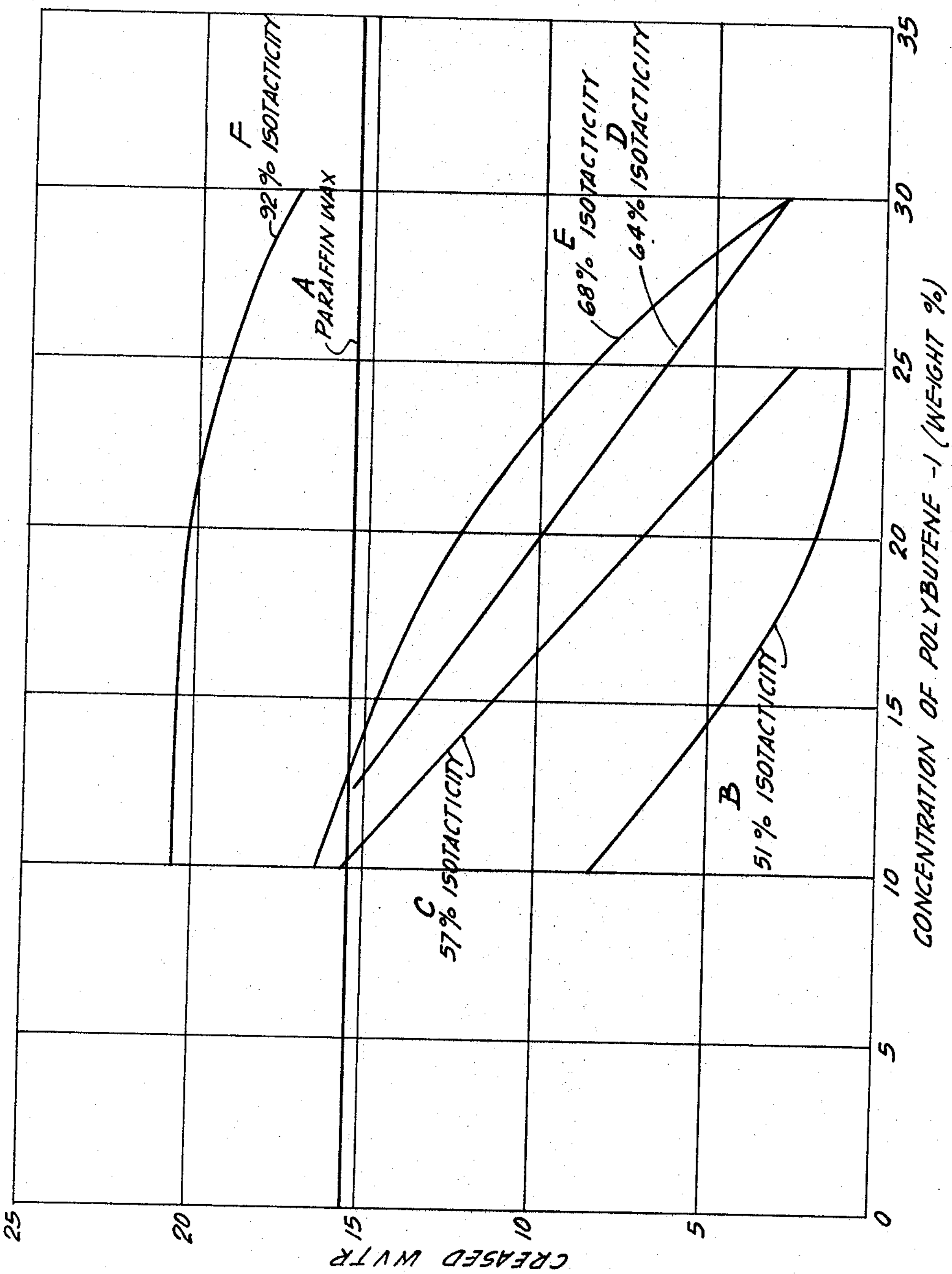

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PARAFFIN WAX POLYBUTENE-1 RESIN BLENDS

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This invention relates to petroleum wax compositions and, more particularly, to petroleum wax coating compositions widely used in forming protective coatings for wrapping paper and paperboard in the production of low-cost cartons for liquids.

It is a principal object of this invention to upgrade refined paraffin waxes with particular reference to improving their creased barrier properties, heat sealing properties and grease resistance.

Other objects and advantages of this invention will be apparent from the following detailed description thereof.

The petroleum industry generally classifies petroleum waxes in three main categories, namely, (1) paraffins; (2) intermediate; and (3) microcrystalline waxes. Other classes of waxes are known such as the scale waxes and slack waxes; these are low-cost crude waxes. The paraffins are predominantly the normal paraffins, i.e., straight chain saturated hydrocarbons with minor amounts of isoparaffins. The microcrystalline waxes are predominantly cyclic saturated hydrocarbons (naphthenes) and isoparaffins. The intermediate waxes are blends or mixtures of paraffin and microcrystalline waxes. In Table I below is given the ranges of certain physical and chemical properties of these three class of waxes.

TABLE I

	Paraffin	Intermediate	Microcrystalline
Melting Point Range, ASTM D127, ° F	120–160	130–160	130–180
Molecular Weight Range	340–400	360–550	500–600
Density Range	0.80–0.917	0.85–0.93	0.89–0.94
Gravity ASTM D287 ° API, 210° F	35–60	30–55	30–50
Distillation, Vacuum Corrected to 760 mm. Hg 5% Point, ° F	750–810	825–900	950–1,050

A typical paraffin wax has the following properties:

Gravity ASTM D287 °API	41.3
Melting point ASTM D87 °F.	140.1
Congealing point ASTM D938 °F.	138.0
Penetration ASTM D1321 at 77° F.	14.0
at 100° F.	40.0
Flash point, °F.	455.0
Ultraviolet absorbtivity at 280 mμ ASTM D2008	0.01
Iodine number	0.4
Molecular weight	442.0
Refractive index	1.4359
Distillation vacuum corrected to 760 mm. Hg 5% point, °F.	804.0

The upgrading of waxes by the addition of additives thereto has sought to improve the creased barrier properties of the coated material. The property of a coating wax employed, for example, in the coating of paper and paperboard, in the manufacture of food wrappers and paper cartons, to minimize passage of moisture vapor through the creased or folded coated paper and paperboard is a most important factor in the commercial acceptance of that coating wax. A standard test widely used in the wax coating art for measuring this property is the creased moisture vapor transmission rate (referred to herein as "creased WVTR"). This test is described in TAPPI 465 creased WVTR. Briefly, it involves the determination

of the weight of water vapor in grams which passes in 24 hours through 100 square inches of accordion pleated test sample containing the specified weight of coating. All values herein for creased WVTR are determined by this test procedure carried out at 100° F. and 95% RH (relative humidity), are truly comparative because the same weight of coating was applied to all test samples (15 pounds per 3000 square feet), and are given in all cases in grams per 100 square inches for a 24 hours test period.

Among other properties sought to be improved by the addition of additives to the wax are the sealing strength of the wax coating and its grease resistance. Sealing strength values are determined by the standard Socony-Vacuum Seal Tester. Two coated specimens which are sealed together under the predetermined temperature, pressure and dwell time specified in the test procedure are pulled at 3 in./min. with a 100 gram load. The values given are the weight in grams required to pull apart the two coated specimens. In the case of the test results given in this specification, the test specimens are each rectangular, 12 inches long, 2 inches wide, arranged in superimposed relation with a 1-inch seal at a temperature of 200–250° F., pressure of 6–10 p.s.i.g. for a dwell time of ¼ to 1.5 minutes.

Grease resistance is a measure of the time required for a drop of the specified grease to penetrate through the coated, uncreased test specimen. The grease used in the test results given herein was Wesson Oil applied at ambient temperature and maintained at 105° F. until failure of the coating.

In accordance with this invention, paraffin waxes are upgraded by blending therewith from 10% to 30% of a polybutene-1 resin having a molecular weight of from 100,000 to 200,000 and an isotactic content of from 50% to 70%. Thus this invention involves wax coating compositions consisting essentially of a paraffin wax blended with from 10% to 30% by weight of a polybutene-1 resin having a molecular weight of from 100,000 to 200,000 and an isotactic content of from 50% to 70%.

In this specification, all percentages are given on a weight basis.

Surprisingly, we have found that the blending wtih paraffin waxes of polybutene-1 resins having an isotactic content of from 50% to 70% and a molecular weight of from 100,000 to 200,000 gives a marked and unexpected improvement in the creased WVTR values and in the heat sealing properties of the blend as well as an improvement in the grease resistance properties. Polybutene-1 resins having higher isotacticities than 70% have markedly poorer creased WVTR values.

The drawing accompanying this specification and forming a part thereof is a graph showing the creased WVTR values plotted against the percent concentration of five different polybutene-1 resins having the different isotactic contents indicated on the graph. In this graph, curve A shows the creased WVTR values for the base paraffin wax, which is a typical paraffin wax having the properties hereinabove given for such wax. Curve B is the graph for a blend of this paraffin wax with a polybutene-1 resin having a moleucular weight of 186,000 and an isotactic content of 51%. Curve C is the graph for a blend of this paraffin wax with a polybutene-1 resin having a molecular weight of 145,000, and an isotactic content of 57%. Curve D is the graph for a blend of this paraffin wax with a polybutene-1 resin having a molecular weight of 151,000 and an isotactic content of 64%. Curve E is the graph for a blend of this paraffin wax with a polybutene-1 resin having a molecular weight of 190,000 and an isotactic content of 68%. Curve F is the graph for a blend of this paraffin wax with a polybutene-1 resin having a molecular weight of 67,000 and an isotactic content of 92%.

It will be noted from FIGURE 1 that the creased WVTR value for the base paraffin wax is 15.5. The blending therewith of polybutene-1 resin having a molecular weight of 186,000 and an isotacticity of 51% markedly improves the creased WVTR values; for a 20% concentration of this polybutene-1 resin the creased WVTR value is reduced to 1.9; and for 25% concentration to 1.0. In the case of polybutene-1 resin having an isotacticity of 57% and a molecular weight of 145,000, a concentration of 20% reduces the creased WVTR value to 7.0, and for 25% concentration to 2.5. In the case of the polybutene-1 resin having a molecular weight of 151,000 and an isotactic content of 64%, blending thereof in a concentration of 20% with the parafin wax base reduces the WVTR value to 10 and for a concentration of 30% of the polybutene-1 resin to 2.7.

Employing a polybutene-1 resin having an isotacticity of 68% the creased WVTR value (16.8) for 10% concentration is slightly higher than the creased WVTR for the base wax; for a 20% concentration the value is 12.6 as compared with 15.5 for the paraffin base wax; and for a 30% concentration the creased WVTR value is 2.7, the same as for the polybutene-1 resin having an isotactic content of 64%.

In the case of polybutene-1 resins having isotactic contents above 70%, e.g., 92%, curve F in the drawing, throughout the range of from 10% to 30% concentration the creased WVTR values are higher than that of the base paraffin wax; at 10% concentration of polybutene-1 resin having an isotactic content of 92% the creased WVTR value is 21.1; at 20% concentration of this resin the creased WVTR value is 20.4 and at 30% concentration the creased WVTR value is 17.6 for this polybutene-1 resin.

The discovery that by blending a polybutene-1 resin having a molecular weight of from 100,000 to 200,000 and an isotactic content of from 50% to 70% in amount of from 10% to 30% by weight, with a paraffin base wax, a wax composition is obtained having improved creased WVTR values and heat sealing properties as compared with the properties of blends of the same paraffin wax with polybutene-1 resins of higher isotactic content, is indeed surprising and unexpected. This phenomenon is peculiar to paraffin base waxes. In the case of other waxes such as the intermediate waxes and microcrystalline waxes, as a general rule, increase in isotacticity of the polybutene-1 resin above 70% used for blending with the wax tends to improve creased WVTR values and the heat sealing properties of the resultant blend. Blends of intermediate and microcrystalline waxes with isotactic polybutene-1 are more fully described in co-pending application Serial No. 395,205, filed September 9, 1964.

In Table II which follows is given the creased WVTR values and sealing strength values for a typical paraffin wax (Atlantic Oil Company's Paraffin 1116). In this table M.W. means molecular weight.

TABLE II

Polybutene-1	Concentration Polybutene-1, Weight Percent	Creased WVTR	Sealing Strength, g./in width
	0	15.5	34
M.W. 186,000, Isotacticity 51%	10	8.5	50
	20	1.9	100
	25	1.0	167
M.W. 145,000 Isotacticity 57%	10	15.4	47
	20	7.0	86
	25	2.5	150
M.W. 151,000 Isotacticity 64%	20	10.0	113
	30	2.7	139
M.W. 190,000, Isotacticity 68%	10	16.8	62
	20	12.6	60
	30	2.7	100
M.W. 67,000, Isotacticity 92%	10	21.1	35
	20	20.4	38
	30	17.6	56

In this specification, the expression "isotactic" is used in its conventional sense to mean the material in the polymer remaining after extraction with diethyl ether; the isotactic material is substantially insoluble in hexane and naphtha. The diethyl ether extraction removes the amorphous or atactic material (which is the material soluble in hexane and naphtha) and leaves a polymer containing the isotactic material.

The polybutene-1 resin employed in forming the wax blends of the present invention can be prepared by polymerizing butene-1 using a Ziegler type catalyst and conducting the polymerization under conditions to produce a polymer having the desired isotactic content of from 50% to 70% and desired molecular weight of from 100,000 to 200,000. Any of the known Ziegler catalysts can be used; for example, catalysts obtained by reaction between compounds of metals of Group IV–A (titanium, zirconium, hafnium or thorium), V–A (vanadium, columbium or tantalum), VI–A (chromium, molybdenum, tungsten or uranium) with alkyl compounds of aluminum or a metal of Group II (beryllium, magnesium, calcium, strontium, barium, zinc or cadmium). Polybutene produced by polymerization using stereospecific catalysts such as CrO_3 or an SIO_2—Al_2O_3 support or a catalyst consisting of a promoted MoO_3 may also be used. In all cases the polymerization must be timed and moderated to produce a polybutene-1 having the desired molecular weight and isotactic content. Hydrogen can be introduced into the polymerization reaction mixture to control the molecular weight and percent isotacticity. Polybutene-1 polymers having an isotactic content of from 50% to 70% and a molecular weight of from 100,000 to 200,000 produced by any known procedure can be used.

Polybutene-1 resins having the above noted isotactic contents and molecular weights blend readily with the paraffin wax.

The blending of polybutene-1 with the paraffin wax can be effected in any known or desired manner. A typical procedure for effecting such blending is described below.

A three-necked flask equipped with an electric drive stirrer, a thermometer, and a nitrogen inlet tube is charged with a measured amount of the wax. The wax is heated under nitrogen with moderate stirring until a clear liquid results. To the melted wax is added a charge of the polybutene-1 resin having the molecular weight and isotacticity and in amount all as herein disclosed. The mixture is heated to a temperature above the melting point of the wax and stirred to assist solution. The mixture can be maintained under a continuous blanket of nitrogen during the heating and stirring, if desired, and particularly when the heating is carried out under higher temperatures than 150° C. The polybutene-1 charge is completely dissolved in the wax in approximately one-half hour; this is evident upon visual inspection. Desirably, however, heating of the blend is continued for an additional one-quarter hour to insure complete dissolution of the resin in the wax. The blend is thereupon allowed to cool to ambient temperature.

Table III which follows gives the grease resistance of blends of paraffin wax with a polybutene-1 resin having a molecular weight of 150,000 and an isotactic content of 64% (hereinafter referred to as PB–1) in concentrations of 20% and 30%. This test was carried out with Wesson Oil applied at ambient temperature and maintained at 105° F. on the uncreased paper.

TABLE III

Blend PB–1:	Time for Grease to Penetrate, i.e., Failure in Hours
20%	3
30%	5

The time for failure to occur in the case of the paraffin wax was one hour. Thus this test shows a marked improvement in grease resistance properties of the blends of this invention as compared with the base paraffin wax.

Examples of this invention have been given in the above including the tables which give comparative data demonstrating the improvements in creased WVTR values and sealing strength of the blends of paraffin wax with polybutene-1 resins having a molecular weight of from 100,000 to 200,000 and an isotactic content of from 50% to 70% as compared with these properties of the base paraffin wax.

The wax blends embodying the present invention are eminently satisfactory for use in existing coating equipment. They can be employed in all fields where wax coatings of superior creased barrier properties, heat seal strength, or good grease resistance, find application. The blends of this invention, in the molten state, can be applied by known coating techniques to foil, parchment, kraft, glassine, chipboard and other paper stocks to produce packaging materials having an attractive gloss and exceptionally good creased vapor barrier.

Since certain changes in the petroleum wax polybutene-1 blends embodying this invention can be made without departing from the scope of this invention, it is intended that all matter contained in the description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A petroleum wax blend consisting of a paraffin wax distilling within the temperature range of about 750–810° F. and from 10% to 30% by weight of a polybutene-1 resin having a molecular weight of from 100,000 to 200,00 and an isotactic content of from 50% to 70% by weight, said blend having creased water vapor transmission rate value less than that of said paraffin wax.

2. A petroleum wax blend of claim **1**, in which the polybutene-1 resin has a molecular weight of about 186,000 and an isotactic content of about 51%.

3. A petroleum wax blend of claim **1**, in which the polybutene-1 resin has a molecular weight of about 145,000 and an isotactic content of about 57%.

4. A petroleum wax blend of claim **1**, in which the polybutene-1 resin has a molecular weight of about 151,000 and an isotactic content of about 64%.

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