

PATENT SPECIFICATION

(11) 1 426 100

1 426 100

- (21) Application No. 27523/73 (22) Filed 8 June 1973
 (31) Convention Application No. 57161/72 (32) Filed 8 June 1972 in (19)
 (33) Japan (JA)
 (44) Complete Specification published 25 Feb. 1976
 (51) INT CL² C08L 57/02
 (52) Index at acceptance
 C3P 102 7D1A 7D1E 7D2A1 7D2A2B 7D2B 7K2 7K7 E2
 PC2 PC8B T2D T2F T2X



(54) A PAINT COMPOSITION

(71) We, MITSUI PETROCHEMICAL INDUSTRIES, LTD., a Japanese Company, of No. 2—5, Kasumigaseki 3-chome, Chiyoda-Ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composition for a hot melt-type white traffic paint having improved flowability during painting.

Hitherto, a hot melt-type white traffic paint composition has been produced by blending a filler such as titanium oxide, glass beads, calcium carbonate, zinc flower or fragmented stone and a binder resin such as a rosin-modified resin or a hydrocarbon resin or a plasticizer such as a vegetable oil, modified alkyd, polybutene or a mineral oil. However, the rosin-modified resin used as a binder resin is not available in unlimited quantities to meet increasing demands because it consists mainly of a natural material. On the other hand, the hydrocarbon resin, represented by petroleum resins has very poor melt flowability when titanium oxide is added thereto (which is essential for the preparation of a white paint). Accordingly, such paints have not been regularly available at low cost. Attempts have been made to improve flowability by using an additive such as stearyl alcohol or lead naphthenate, but have not proved satisfactory. Rather, the result has been a loss of whiteness or an increase of viscosity.

It has been found that in order to improve the melt flowability of conventional hydrocarbon resins, and to obtain a white paint containing titanium oxide having suitable properties as a traffic paint, it is necessary to modify the hydrocarbon resin by introducing a polar portion thereto to a moderate degree, thereby to increase the dispersibility therein of titanium dioxide, which is a polar pigment.

According to the present invention there is provided a composition for a hot melt-type white traffic paint comprising (A) at least

one of an acid-modified hydrocarbon resin having an acid value of 0.10 to 15 obtained from a thermoplastic hydrocarbon resin which is solid at room temperature and has an average molecular weight of 500 to 3000, a softening point of 60 to 150° C. as determined by the ring ball method and a Gardner colour of not greater than 10, as measured for 100% resin, or an ester-bodified hydrocarbon resin obtained by the reaction of said acid-modified hydrocarbon resin with an alcohol, and (B) titanium dioxide.

The hydrocarbon resins used in this invention include thermoplastic hydrocarbon resins such as, for example, a petroleum resin obtained by polymerizing in the presence of a Friedel-Crafts catalyst fractions having a boiling point of from 15 to 280° C. at atmospheric pressure formed by the thermal cracking of petroleum. Generally, heavy petroleum fractions such as light naphtha, heavy naphtha and gas oil may be cracked in a short time and under a comparatively low pressure in the presence of steam at a temperature of from 500° to 900° C. Hydrocarbons derived from such a steam cracking process usually contain a large amount of diolefins, olefins, aromatic hydrocarbons and some paraffins. Of the fractions defined as having a boiling point of from 15 to 280° C., preferred are those which contain 30 to 60% olefins, 10 to 30% diolefins, 20 to 50% aromatics, 5 to 20% paraffins and naphthenes, totalling 100%, produced by such a process.

As olefins, aliphatic hydrocarbons having 4 to 5 carbon atoms and aromatic vinyl hydrocarbons such as styrene (C₈), α -methylstyrene, (C₉), vinyltoluene (C₉) and indene (C₉) are preferably used.

Of the aforesaid materials, an aliphatic petroleum resin obtained by polymerizing a fraction containing aliphatic olefins and diolefins of from C₄ to C₁₀, or a hydrogenated product of an aromatic petroleum resin which is obtained by polymerizing a fraction (mainly C₆ fraction) having a boiling point of 140 to 280° C., is most preferred as the raw material.

50

55

60

65

70

75

80

85

90

95

Friedel-Crafts catalysts such as aluminium trichloride, aluminium trichloride-aromatic hydrocarbon complexes, aluminium tribromide, boron trifluoride, boron trifluoride-phenol complex, titanium chloride, ethyl aluminium chloride and ferric chloride are used with success.

These catalysts may be used in the solid, liquid or gaseous state, but it is most convenient to use them in the form of a liquid. Although the amount of catalyst may be varied, it is most practical to use these catalysts in an amount of from 0.5 to 3.0% by weight of the unsaturated hydrocarbon raw material.

The polymerization temperature may be varied in a wide range, but a preferred temperature is from -80 to $120^{\circ}\text{C}.$, most preferably from -10 to $80^{\circ}\text{C}.$ In order to carry out the polymerization at a high temperature, it is necessary to use a polymerization vessel which is pressure resistant. The polymerization time is normally from 1 to 5 hours.

Hydrocarbon resins obtained by the cationic or radical polymerization of styrenes such as styrene, α -methyl styrene, vinyl toluene, or isopropenyl toluene may also be used with success. Styrene derivatives, which are aromatic hydrocarbons having 8 to 10 carbon atoms and further containing a vinyl group, are preferably used in the present invention (blends of styrene derivatives can be used). Cationic polymerization is preferably conducted with a Lewis acid such as BF_3 , AlCl_3 , TiCl_4 , EtAlCl_2 and FeCl_3 , or a protonic acid such as HClO_4 present in an amount of from 0.1 to 2% by weight of the unsaturated hydrocarbon raw material in a solvent such as aliphatic hydrocarbons of C_5 to C_{10} such as hexane or heptane, aromatic hydrocarbons such as benzene, toluene or xylene or halogenated aromatic hydrocarbons such as chlorobenzene at a temperature of from -50 to $50^{\circ}\text{C}.$ for from 0.5 to 5 hours.

Radical polymerization may be conducted in an excellent manner using a catalyst such peroxide (B.P.O.), dicumyl peroxide (D.C.P.) or ditertiarybutyl peroxide (D.T.P.) in an amount of from 0.1 to 1% by weight of the unsaturated hydrocarbon raw material at a temperature of from 60 to $160^{\circ}\text{C}.$ for from 3 to 8 hours in a solvent such as an aromatic hydrocarbon, e.g. benzene, toluene or xylene.

Hydrogenated products of the above resins can also be used. The degree of hydrogenation of the aromatic ring (which can be measured by means of the ultraviolet spectrum) may be from 0 to 100%, preferably from 30 to 60%.

Hydrogenation may be performed at a reaction temperature of from 150 to $250^{\circ}\text{C}.$ (preferably, from 200 to $250^{\circ}\text{C}.$), at a reaction pressure (hydrogen-pressure) of from 30 to 250 Kg/cm^2 (preferably, from 500 to

100 Kg/cm^2), using a catalyst such as nickel (carrier: diatomaceous earth, alumina, silica gel, pumice; Raney nickel, etc.) in a solvent such as aliphatic saturated hydrocarbons such as hexane, or heptane.

It will be appreciated by one skilled in the art that the above parameters are not limitative, but can be widely varied by one skilled in the art outside of the above ranges to obtain acceptable results. However, these ranges are the results of extensive experimentation by the inventors based upon their skill in this art, and accordingly will, in general, provide excellent results.

Of the above petroleum resins, the aliphatic petroleum resins obtained by polymerizing fractions having a boiling point of -15° to $60^{\circ}\text{C}.$ at atmospheric pressure (formed by the thermal cracking of petroleum) using a Friedel-Crafts catalyst are especially preferred because they have superior reactivity during modification as described below and give modified products of good thermal resistance and colour.

This fraction having a boiling point of -15 to $60^{\circ}\text{C}.$ comprises cracked mainly unsaturated aliphatic hydrocarbons having 4 to 5 carbon atoms such as butene, butadiene, pentene and pentadiene. The composition of such a fraction may be as follows:

C_4 and C_5 olefins	40 to 70 wt. %
C_4 and C_5 diolefins	20 to 60 "
Paraffins	10 to 30 "

The composition of the C_4 and C_5 Fraction (Polymerizable Monomer) of the above fraction is as follows:

C_4 1-butene	10.6%
C_4 2-butene	9.6
C_4 isobutene	15.3
C_4 1,3-butadiene	18.3
C_5 1-pentene	2.6
C_5 2-pentene	3.2
C_5 cyclopentene	2.1
C_5 1,3-piperylene	3.0
C_5 isoprene	6.3
C_5 cyclopentadiene	4.7
C_5 2-methyl-1-butene	3.7
C_5 2-methyl-2-butene	2.1

Hydrogenation products of petroleum resins obtained by polymerizing a fraction containing 30 to 60 weight % of aromatic vinyl hydrocarbons such as styrene, α -methylstyrene and indene which is obtained by means of the decomposition of petroleum and has a boiling point of 140 to $280^{\circ}\text{C}.$, in the presence of a Friedel-Crafts catalyst, or resins obtained by radical- or cation-polymerization of styrene, α -methylstyrene or isopropenyl toluene, are also preferred raw materials because of their superior thermal resistance.

All these hydrocarbon resins are solid at

room temperature, and have an average molecular weight of from 500 to 3000, preferably from 700 to 2000, a softening point (as measured by the ring ball method) of 60 to 150° C., preferably 70 to 120° C., and a colour (Gardner, resin 100%) of not more than 10, preferably not more than 8 and most preferably greater than 1.

As will be shown in the Comparative Examples hereinafter, these hydrocarbon resins, when blended with titanium oxide, have extremely poor flowability at the time of melting, and it is difficult or even impossible to paint with such a composition. Accordingly, the hydrocarbon resins must be modified.

One effective method is to introduce a polar moiety into the hydrocarbon resin by oxidizing it. This can be accomplished by various methods. In order to oxidize the hydrocarbon resin uniformly and to obtain a product of good colour, it is recommended to employ a method wherein air or oxygen is blown into the hydrocarbon resin in the liquid state, for instance in the molten state. If a radical initiator, e.g., dicumyl peroxide or ditertiarybutyl peroxide is used at this time, the time required for the reaction can be shortened, but the use of the radical initiator is not essential. When the hydrocarbon resin is modified by such a method to adjust its acid value to at least 0.10, the flowability of a blend thereof with titanium oxide is greatly increased. Since excessive oxidation results in poor colour, the acid value of the modified product should be adjusted to not more than 15. The oxidation reaction proceeds most smoothly at a pressure of from atmospheric pressure to 10 atmospheres and at a temperature of 100 to 230° C., with the reaction generally being completed in from 15 minutes to 5 hours. The rate of oxygen feed is most preferably maintained at 20 to 50 l/hr per mole of hydrocarbon resin. The modification with an α,β -unsaturated acid or an anhydride thereof proceeds smoothly at a pressure of from atmospheric pressure to 10 atms., preferably 1 to 2 atms., at a temperature of 150 to 230° C., preferably 180 to 220° C., and within 15 minutes to 5 hours, preferably 30 minutes to 2 hours.

It is also effective to introduce a polar moiety by reacting the hydrocarbon resin with an α,β -unsaturated carboxylic acid or an anhydride thereof. Of these materials, most preferred are those with 3 to 6 carbon atoms since they provide especially excellent results. This method is especially preferred since it results in products having better colour than in the case of the oxidation method. Examples of the α,β -unsaturated carboxylic acid that can be used are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, maleic anhydride, itaconic anhydride, and citraconic anhydride. Mixtures thereof can be used, if desired. It is also

possible to add the α,β -unsaturated carboxylic acid to the hydrocarbon resin with heating to form an addition product. Where the reaction temperature is low or the reaction time is short, an ordinary radical initiator, e.g., dicumyl peroxide or ditertiarybutyl peroxide, may be used. For example, the hydrocarbon resin, which is a raw material, is melted at 150 to 230° C. and then from 0.01 to 5 parts by weight of the α,β -unsaturated carboxylic acid or anhydride thereof are added to 100 parts by weight of the resulting hydrocarbon resin while stirring at a pressure of from normal to 10 atms., preferably normal pressure, at from 150 to 230° C., preferably 180 to 220° C., for from 15 minutes to 5 hours.

If a radical initiator such as dicumyl peroxide is used, the reaction is carried out at 160 to 210° C. for 15 minutes to one hour.

When there is unreacted carboxylic acid present, it is preferred to remove it to concentrate the reaction product. Unreacted carboxylic acid can be removed by heating under reduced pressure. For example, if maleic anhydride is used, the heating may be carried out at 200° C./10 mmHg. If too much α,β -unsaturated carboxylic acid is reacted, the colour of the acid-modified hydrocarbon resin becomes poor, and the product is not preferred for use in a white paint. Accordingly, the amount of the α,β -unsaturated carboxylic acid is preferably from 0.01 to 5 parts by weight per 100 parts by weight of the hydrocarbon resin (incorporation is substantially stoichiometric). When the α,β -unsaturated carboxylic acid is reacted in such an amount, there will be obtained an acid-modified hydrocarbon resin having an acid value of 0.10 to 15. The flowability of the resulting product upon melting is better than that of an oxidized hydrocarbon resin.

The modification with an α,β -unsaturated acid or an anhydride thereof proceeds smoothly at a pressure of from atmospheric pressure to 10 atms., preferably 1 to 2 atms., at a temperature of 150 to 230° C., preferably 180 to 220° C., and within 15 minutes to 5 hours, preferably 30 minutes to 2 hours.

It is also effective to introduce an ester bond by further reacting the acid-modified hydrocarbon resin thus obtained with an alcohol. The resulting product has improved thermal stability at high temperatures. Examples of the alcohol are monohydric alcohols such as methanol, ethanol, propanol, or butanol and polyhydric alcohols such as ethylene glycol, propylene glycol, butanediol or glycerol. Preferred, are those mono- or polyalcohols having up to 5 carbon atoms, and most preferred are mono-, di-, or trihydric alcohols having 1 to 5 carbon atoms. Mixtures thereof can, of course, be used, if desired.

The ester-modified or esterified hydrocarbon resin may be obtained by heating the alcohol

together with the acid-modified hydrocarbon resin at 160 to 250° C. for 1 to 5 hours for example, at an elevated pressure or at atmospheric pressure. When the amount of alcohol is from 0.3 to 50% by weight of acid-modified resin, and the saponification degree is 0.10 to 30, preferably 1 to 20, a most preferred product is obtained.

The blending of these modified hydrocarbon resins with titanium dioxide is preferably performed by melting the modified resin and then adding titanium dioxide powder with stirring. A temperature of 180 to 220° C. is representative of generally used blending conditions. A suitable amount of titanium dioxide added is 25 to 300 parts by weight per 100 parts by weight of the modified resin. Most excellent results are obtained with titanium dioxide of a particle size of 0.01 to 5 microns, preferably 0.01 to 0.50 microns.

Another filler and/or a plasticizer can also be incorporated therein, if desired, in order to use the resulting composition as a traffic paint. Examples of such other fillers are calcium carbonate, glass beads, cracked stone and zinc white, in an amount of 40% to 75% by weight, with useful plasticizers including mineral oil, polybutene, soybean oil and vegetable oil-modified alkyd material in an amount of from 1 to 5% by weight. In such a case, the titanium dioxide is preferably used in an amount of from 5 to 30% and the modified resin in an amount of from 10 to 30% by weight (to total 100%).

While the above discussion has been primarily in terms of using one resin, it will be clear that mixtures of various different resins from various classes as defined above can be used to obtain a balance of various beneficial properties thereof.

The present invention will now be described in greater detail by reference to the following Examples and Comparative Examples in which the test methods employed upon the titanium dioxide-containing compositions were as follows:

(A) Preparation of the Titanium Dioxide-Containing Composition:—

A 500 ml beaker containing 300 g of the modified resin was immersed in a constant temperature oil bath held at 205° C. When the resin was almost melted, it was stirred and 300 g of titanium dioxide powder (TIPAQUE A—220, Registered Trade Mark, product of Ishihara Sangyo Kaisha Ltd.; particle size of from 0.15 to 0.25 μ) was added over the course of 10 minutes with stirring.

(B) Method of Measuring Flowability:—

10 minutes from the time when the temperature of the titanium dioxide-blended composition reached 180° C., the flowability of the composition was measured. (Composition interior temperature 185 to 195° C.). The

titanium dioxide-blended composition was removed with a tubular metal spoon of a diameter of 31 mm and a length of 24 mm, and quickly dropped onto a smooth stainless steel plate from a height of 45 mm. The long axis (a) and the short axis (b) of the disc-like blended composition on the plate were measured, and the flowability expressed by the average value [$\frac{1}{2}(a+b)$].

(C) Melt Viscosity:—

After the measurement of the flowability, it was confirmed that the composition interior temperature was from 185 to 195° C. The melt viscosity of the composition was then measured by a B-type rotary viscometer (Vismetron, product of Tokyo Keiki).

(D) Whiteness:—

The whiteness of the composition in disc form as obtained in (B) above was visually evaluated by the naked eye, and ranked as A, B, C, D, E in the order of superior whiteness.

EXAMPLE 1.

500 g of an aliphatic hydrocarbon resin, softening point (ring ball method) 97.5° C., average molecular weight 1,620, colour 5 (Gardner), acid value 0.06 was synthesized as follows: the following C₅ fraction* having a boiling point of 30 to 45° C. obtained by cracking petroleum was reated at 120° C. for 1 to 3 hours, cyclopentadiene (C.P.D.) was further removed by dimerization, and then the content of cyclopentadiene was limited to less than 3%.

*C₅ fraction composition

1-pentene	4.8%	
1,3-pentadiene	9.1	100
2-methyl-1-butene	7.2	
cyclopentadiene	9.3	
2-pentene	4.9	
3-methyl-1-butene + isopentane	12.0	
2-methyl-2-butene	3.5	105
isoprene	14.7	
others	34.5	

It was then used as the raw material and polymerized in the presence of 10 ml/100 g C₅ of an AlCl₃-xylene slurry (complex) as a catalyst at 50 to 80° C. for about 3 hours and then melted at 180° C., and oxidized at 180° C. at atmospheric pressure by blowing air thereinto with stirring at a flow rate of 30 l/hour for 1 hour. The resulting resin had a softening point of 99° C., a colour of 8 to 9, and an acid value of 0.2. A blended composition thereof with titanium dioxide was prepared. In more detail, a 500 ml beaker containing 300 g of this modified resin was immersed in a constant temperature oil bath held at 205° C. When the resin was almost melted, it was stirred and 300 g of titanium dioxide powder (TIPAQUE A—220,

product of Ishihara Sangyo Kaisha Ltd. having particle size of 0.15 to 0.25 micron) was added over the course of 10 minutes with stirring. Unless otherwise indicated, all blended compositions of the invention described in the following examples were so prepared. The blended composition was then tested. The results are shown in the Table hereinafter.

EXAMPLE 2.

500 g of the same aliphatic hydrocarbon resin as was used in Example 1 was melted at 210° C., and 5 g of maleic anhydride was added thereto with stirring at 210° C. at atmospheric pressure to react them for one hour. The resulting resin was free from the odour of maleic anhydride, and had a softening point of 98° C., a colour of 5 and an acid value of 4.8. A blended composition thereof with titanium dioxide was prepared, and tested. The results are shown in the Table hereinafter.

EXAMPLES 3 to 5.

Example 2 was repeated except that the amount of maleic anhydride was varied. The results are shown in the Table hereinafter.

EXAMPLE 6.

500 g of the same modified hydrocarbon resin as was obtained in Example 2 and 10 g of *n*-butanol were reacted (esterification) at 180° C. for 2 hours at atmospheric pressure in a closed vessel, and the unreacted matter was removed. There was obtained a modified hydrocarbon resin containing an ester bond and having a softening point of 98° C., a colour of 5, an acid value of 1.5 and a saponification value of 8.0. A composition obtained by blending this modified resin with titanium dioxide was tested, and the results are shown in the Table hereinafter.

COMPARATIVE EXAMPLE 1.

A composition was prepared by blending the starting resin used in Example 1 with titanium dioxide. The blended composition was tested, and the results are shown in the Table. No flowability of the composition at the time of melting was observed.

COMPARATIVE EXAMPLE 2.

Comparative Example 1 was repeated except that 3.3% by weight of stearyl alcohol was further added as a wetting agent for the titanium dioxide. The results are shown in the Table. It was seen that the resulting composition had improved flowability, but poor whiteness. The effectiveness of the present invention can be seen clearly by comparing Examples 1 to 4 with Comparative Examples 1 and 2.

EXAMPLE 7.

1 kg of an aromatic hydrocarbon resin

[Petrozin #120, product of Mitsui Petrochemical Industries, Ltd., softening point 120° C. (ring ball method), average molecular weight 870, colour 12 (Gardner), acid value 0.10] was dissolved in 1 kg of hexane, and the solution was charged into a 10-litre autoclave with 60 g of a nickel-diatomaceous earth catalyst (Ni 50%, diatomaceous earth 48%, graphite 2%; preparation: Diatomaceous earth which had been purified by nitric acid was added to an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and then nickel carbonate was precipitated on the diatomaceous earth by ammonium carbonate.) The mixture was stirred for 6 hours at 200 to 250° C. and at a hydrogen partial pressure of 70 Kg/cm² to hydrogenate the resin.

The catalyst was removed by passing the product through a glass filter, and then the solvent and the volatile component were removed. There was obtained a hydrogenated hydrocarbon resin having a softening point of 115° C., a colour of not more than 1 and an acid value of 0.05.

500 g of the hydrogenated hydrocarbon resin and 5 g of maleic anhydride were reacted for 2 hours at 200° C. in the presence of 2 g of ditertiary butyl peroxide to provide a modified resin having a softening point of 115° C., a colour of 2 and an acid value of 4.9.

A composition prepared by blending the resulting modified resin with titanium dioxide was tested. The results are shown in the Table hereinafter.

COMPARATIVE EXAMPLE 3.

A composition prepared by blending (as in Example 1) the starting aromatic hydrocarbon resin used in Example 7 was tested. The results are shown in the Table hereinafter.

COMPARATIVE EXAMPLE 4.

A composition prepared by blending the hydrogenated hydrocarbon resin intermediate of Example 7 with titanium dioxide was tested. The results are shown in the Table. It is seen from a comparison of Example 7 with Comparative Examples 3 and 4 that the present invention is effective. Especially in Comparative Example 3, the resulting composition was found to be unsuitable as a white paint because of its poor heat stability and colour.

EXAMPLE 8.

A three-necked flask was charged with 250 g of styrene, 250 g of vinyl toluene and 500 g of toluene, and a boron trifluoride-phenol complex [boron trifluoride (30%)-phenol (70%); 2% by weight based on total reactants] was added little by little with stirring. The reaction was performed for 3 hours at 20° C. while cooling the flask with a dry ice-acetone bath. The catalyst was removed

with an alkali, and the reaction mixture was concentrated in order to drive off solvent and unreacted monomers. There was obtained a styrene/vinyl toluene copolymer having a softening point of 102° C., a colour of not more than 1, an average molecular weight of 1,400 and an acid value of 0.01.

500 g of the copolymer, 5 g of maleic anhydride and 3 g of ditertiary butyl peroxide were heated to a temperature of from 180° C. to 210° C. and the reaction was performed with stirring for 2 hours to afford a modified resin having a softening point of 103° C., a colour of 2 and an acid value of 4.60.

A composition prepared by blending the resulting modified copolymer with titanium dioxide was tested. The results are shown in the Table hereinafter.

COMPARATIVE EXAMPLE 5.

A composition prepared by blending the copolymer used in Example 8 with titanium dioxide was tested. The results are shown in the Table hereinafter. The effectiveness of the

present invention can be clearly seen from the results obtained.

EXAMPLE 9.

A 2 l beaker containing 200 g (20 wt.%) of the same resin as was used in Example 2 was immersed in a constant temperature oil bath held at 205° C. When the resin was almost melted, it was stirred and 150 g (15 wt.%) of titanium dioxide having a particle size of 0.15 to 0.25 micron, 640 g (64 wt.%) of calcium carbonate and 10 g (1 wt.%) of soybean oil was added over the course of 10 minutes with stirring to form a white traffic paint. The results are shown in the Table hereinafter.

COMPARATIVE EXAMPLE 6.

Example 9 was repeated except that an aliphatic unmodified hydrocarbon resin as was used in Example 1 was used in place of the acid-modified resin. The results are shown in the Table hereinafter.

TABLE

	Method of modification (wt. %)	Flowability (mm)	Melt viscosity (poises)	Whiteness	Acid value of the resin
Example 1	Air oxidation	64.5	144	A	0.20
2	Maleic anhydride (1)	68.1	90	A	4.80
3	" (5)	62.4	100	A - B	13.0
4	" (0.2)	67.5	60	A	1.1
5	" (0.01)	64.5	120	A	0.15
6	Esterification	67.8	100	A	1.50
Comparative Example 1		0	more than 2 million	-	0.06
Comparative Example 2	Adding stearyl alcohol	52.1	500	B	0.06
Example 7	Maleic anhydride (1)	65.6	80	A	4.90
Comparative Example 3		0	44,000	E	0.08
Comparative Example 4		0	more than 2 million	A - B	0.05

TABLE (Continued)

	Method of modification (wt. %)	Flowability (mm)	Melt viscosity (poises)	Whiteness	Acid value of the resin
Example 8	Maleic anhydride (1)	65.2	90	A	4.60
Comparative Example 5		40.5	38,000	A	0.01
Example 9		58.8	270	A	
Comparative Example 6		0	2,000,000	—	

WHAT WE CLAIM IS:—

1. A composition for a hot melt-type white traffic paint comprising (A) at least one of an acid-modified hydrocarbon resin having an acid value of 0.10 to 15 obtained from a thermoplastic hydrocarbon resin which is solid at room temperature and has an average molecular weight of 500 to 3000, a softening point of 60 to 150° C. as determined by the ring ball method and a Gardner colour of not greater than 10, as measured for 100% resin, or an ester-modified hydrocarbon resin obtained by the reaction of said acid-modified hydrocarbon resin with an alcohol, and (B) titanium dioxide.
2. A composition according to Claim 1, wherein said acid-modified hydrocarbon resin is obtained by the oxidation of said thermoplastic hydrocarbon resin.
3. A composition according to Claim 2, wherein said oxidation is carried out at a pressure of from atmospheric to 10 atmospheres, at a temperature of from 100 to 230° C. for from 15 minutes to 5 hours with an oxygen feed rate of from 20 to 50 1/hr/mole of hydrocarbon resin.
4. A composition according to Claim 3, wherein the temperature of oxidation is from 180 to 220° C.
5. A composition according to Claim 1, wherein said acid-modified hydrocarbon resin is obtained by the reaction of said thermoplastic hydrocarbon resin with an α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic acid anhydride having 3 to 6 carbon atoms.
6. A composition according to Claim 5, wherein said α,β -unsaturated carboxylic acid

TABLE (Continued)

	Method of modification (wt. %)	Flowability (mm)	Melt viscosity (poises)	Whiteness	Acid value of the resin
Example 8	Maleic anhydride (1)	65.2	90	A	4.60
Comparative Example 5		40.5	38,000	A	0.01
Example 9		58.8	270	A	
Comparative Example 6		0	2,000,000	-	

WHAT WE CLAIM IS:—

1. A composition for a hot melt-type white traffic paint comprising (A) at least one of an acid-modified hydrocarbon resin having an acid value of 0.10 to 15 obtained from a thermoplastic hydrocarbon resin which is solid at room temperature and has an average molecular weight of 500 to 3000, a softening point of 60 to 150° C. as determined by the ring ball method and a Gardner colour of not greater than 10, as measured for 100% resin, or an ester-modified hydrocarbon resin obtained by the reaction of said acid-modified hydrocarbon resin with an alcohol, and (B) titanium dioxide.
2. A composition according to Claim 1, wherein said acid-modified hydrocarbon resin is obtained by the oxidation of said thermoplastic hydrocarbon resin.
3. A composition according to Claim 2, wherein said oxidation is carried out at a pressure of from atmospheric to 10 atmospheres, at a temperature of from 100 to 230° C. for from 15 minutes to 5 hours with an oxygen feed rate of from 20 to 50 l/hr/mole of hydrocarbon resin.
4. A composition according to Claim 3, wherein the temperature of oxidation is from 180 to 220° C.
5. A composition according to Claim 1, wherein said acid-modified hydrocarbon resin is obtained by the reaction of said thermoplastic hydrocarbon resin with an α,β -unsaturated carboxylic acid or α,β -unsaturated carboxylic acid anhydride having 3 to 6 carbon atoms.
6. A composition according to Claim 5, wherein said α,β -unsaturated carboxylic acid

25

30

35



- or acid anhydride reacted with said hydrocarbon resin is selected from maleic acid, fumaric acid, itaconic acid, citraconic acid, acrylic acid, methacrylic acid, maleic anhydride, itaconic anhydride, citraconic anhydride or a mixture of two or more thereof.
7. A composition according to Claim 5 or 6 wherein said α,β -unsaturated carboxylic acid or acid anhydride is used in an amount of 0.01 to 5 parts by weight per 100 parts by weight of the hydrocarbon resin.
8. A composition according to Claim 1, wherein said alcohol reacted with the acid-modified hydrocarbon resin is a mono-, di- or trihydric alcohol having 1 to 5 carbon atoms.
9. A composition according to Claim 8, wherein said alcohol is selected from methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butanediol, glycerol or a mixture thereof.
10. A composition according to Claim 8 or 9, wherein said alcohol is reacted with the acid-modified hydrocarbon resin in an amount of from 0.3 to 50% by weight thereof and to a saponification degree of from 0.10 to 30.
11. A composition according to any preceding Claim, wherein said hydrocarbon resin is a petroleum resin obtained by polymerizing a thermally cracked petroleum fraction having a boiling point of from -15 to 280°C . in the presence of a Friedel-Crafts catalyst.
12. A composition according to any of Claims 1 to 10, wherein said hydrocarbon resin is prepared by hydrogenating a petroleum resin obtained by polymerizing an aromatic rich hydrocarbon fraction having a boiling range of 140 to 280°C . obtained by thermal cracking of petroleum in the presence of a Friedel-Crafts catalyst.
13. A composition according to any of Claims 1 to 10, wherein said hydrocarbon resin is prepared by polymerizing a C_4 to C_6 fraction obtained by thermal cracking having a boiling point of -15 to 60°C ., mainly composed of unsaturated aliphatic hydrocarbons having four to five carbon atoms in the molecules thereof, in the presence of a Friedel-Crafts catalyst.
14. A composition according to any preceding Claim, wherein said titanium oxide is present in an amount of from 25 to 300 parts by weight per 100 parts by weight of the acid-modified hydrocarbon resin or the ester-modified hydrocarbon resin.
15. A composition according to any preceding Claim, wherein said titanium dioxide has an average particle size of from .01 to 5 microns.
16. A composition according to Claim 15, wherein the particle size is from .01 to .50 microns.
17. A composition according to any preceding Claim, which further comprises a filler and/or a plasticizer.
18. A composition according to Claim 17, wherein the filler is calcium carbonate, glass beads, cracked stone or zinc white.
19. A composition according to Claim 17 or 18, wherein said filler is present in an amount of 40% to 75% by weight.
20. A composition according to Claim 17, wherein the plasticizer is mineral oil, polybutene, soyabean oil or vegetable oil modified alkyl material.
21. A composition according to Claim 17 or 20, wherein the plasticizer is present in an amount of from 1 to 5% by weight.
22. A composition according to any of Claims 17 to 21, wherein the titanium dioxide is present in an amount of from 5 to 30% and the modified-resin in an amount of from 10 to 30% by weight.
23. A composition for a hot melt-type white traffic paint according to Claim 1, substantially as hereinbefore described with reference to any of the foregoing Examples 1 to 9.
24. A hot melt-type white traffic paint which comprises a composition as claimed in any preceding claim.

GEE & CO.,
Chartered Patent Agents,
Chancery House,
Chancery Lane,
London, WC2A 1QU, and
39, Epsom Road,
Guildford, Surrey.
Agents for the Applicants.