

PATENT SPECIFICATION

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 2L7 2L8



(54) METHOD OF COLOURING SYNTHETIC RESIN MATERIAL

(71) We, KABUSHIKI KAISHA DAINI SEIKOSHA, a Japanese company of 31—1, 6-chome, Kameido, Koto-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 methods of colouring synthetic resin material and to synthetic resin material coloured thereby.

Conventionally, the surface of synthetic resin material is colouring by painting, printing or dyeing processes. Alternatively, a coloured pigment may be introduced in the body of the synthetic resin material. If a synthetic resin material is coloured by a painting or printing process, it becomes opaque and loses brightness and surface smoothness. If the synthetic resin material is coloured by a dyeing process its surface becomes swollen and this swelling has to be removed by a subsequent time-consuming process. If a coloured pigment is included in the body of the synthetic resin material it is difficult to achieve a desired colour tone due to the fact that the pigment must be added to the raw material of the synthetic resin material. Thus only relatively large quantities of synthetic resin material are made by this method and this is disadvantageous from the point of view of economy.

According to one aspect of the present invention, there is provided a method of colouring synthetic resin material comprising the steps of immersing the synthetic resin material in a colouring solution which is at a temperature less than the softening temperature of the synthetic resin material, the colouring solution comprising, in admixture, 0.1% to 50% by weight of at least one polyacid having a general formula:



where n is an integer between 3 and 15, 5% to 60% by weight of at least one polyhydric alcohol, a dye, and water.

In the preferred Examples the or each polyacid is one of adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, Brasilic and tetradecanedioic acid.

The at least one polyhydric alcohol may be a dihydric alcohol. Thus the or each dihydric alcohol may be of ethylene glycol, propane-1,2-diol, butanediol, pentanediol and hexanediol.

Alternatively the at least one polyhydric alcohol may be a trihydric alcohol. The trihydric alcohol may be glycerin.

Preferably the synthetic resin material is immersed in the colouring solution, which is at a temperature between 50°C and 95°C, for less than 5 minutes.

Preferably the colouring solution contains between 1% and 15% by weight of the at least one polyacid.

Preferably the colouring solution contains between 25% and 30% by weight of the at least one polyhydric alcohol.

Preferably the colouring solution contains between 1% and 3% by weight of dye.

According to a further non restrictive aspect of the present invention there is provided a synthetic resin material when coloured by the method recited above.

The invention will be illustrated with reference to the following Examples.

EXAMPLE 1

A colouring solution having the following constituents in admixture:

	by weight	
suberic acid	13.0%	80
ethylene glycol	26.0%	
water	60.0%	
blue dye (sold under the trade mark Sumikaron Navy Blue S-2GL)	1.0%	85

was maintained at 8°C, and an exudative article made of an acrylate resin material was immersed therein for 1-1/2 minutes. After removing the article from the colouring solution, it was washed in water and dried. It was found that the article was uniformly coloured

blue and was as hard, bright and transparent as prior to colouring.

EXAMPLE 2

A colouring solution having the following constituents in admixture:

	by weight
azelaic acid	2.0%
ethylene glycol	29.0%
water	68.0%
red dye (sold under the trade mark Sumikaron Red S-GG)	1.0%

was maintained at 68°C and an exudative article made of an acrylate resin material was immersed therein for three minutes. The articles was subsequently treated in the same manner as the article in Example 1. It is found that the article was uniformly coloured red and was as hard, bright and transparent as prior to colouring.

EXAMPLE 3

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	1.3%
ethylene glycol	28.2%
water	69.3%
yellow dye (sold under the trade mark Sumikaron Yellow SE-5G)	1.2%

was maintained at 68°C and an exudative article made of an acrylate resin material was immersed therein for 45 seconds. The article was subsequently treated in the same manner as the article of Example 1. It was found that the article was uniformly coloured yellow and was as hard, bright and transparent as prior to colouring.

EXAMPLE 4

A colouring solution having the following constituents in admixture:

	by weight
azelaic acid	1.5%
1,3-propanediol	26.5%
water	71.0%
green dye (sold under the trade mark Kayalon Fast Brilliant Green B)	1.0%

was maintained at 83°C, and a sheet of polyester film ("Mylar"—trade mark) was immersed therein for four minutes. After removing the film from the colouring solution, it was washed in water and dried. It is found that the film was informly coloured green and was as hard, bright and as transparent as prior to colouring.

EXAMPLE 5

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	1.5%
1,3-propanediol	26.5%
water	71.0%
blue dye (sold under the trade mark Kayalon Brilliant Blue G)	1.0%

was maintained at a temperature of 90°C an exudative article made of epoxy resin material was immersed therein for three and one half minutes. After removing the article from the colouring solution, it was washed in water and dried. It was found that the article was uniformly coloured dark blue and was as hard and bright as prior to colouring.

EXAMPLE 6

A colouring solution having the following constituents in admixture:

	by weight
suberic acid	50%
ethylene glycol	14%
water	35%
blue dye (sold under the trade mark Kayalon Poly- ester Turquoise Blue GGF)	1%

was maintained at 68°C, although crystals could be seen in the colouring solution. An exudative article made of an acrylate resin material was immersed in the colouring solution for four minutes. When the article was removed from the colouring solution, crystals of suberic acid were attached to the surface thereof. After washing and drying, it was found that the article was coloured blue and was as hard, bright and transparent as prior to colouring. It was found that if the quantity of suberic acid was increased, the quantity of crystals attached to the surface of the article on removal from the colouring solution was increased. The removal of these crystals caused problems and so it is preferable from a practical point of view that the amount of suberic acid in the colouring solution is limited.

EXAMPLE 7

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	1.3%
ethylene glycol	28.2%
water	69.3%
blue dye (sold under the trade mark Sumikaron Blue E-GRL)	1.2%

was maintained at a temperature of 70°C and an exudative article made of a polyacetal resin was immersed therein for one minute. After removing the article from the colouring solution it was washed in water and dried. It was found that the article was uniformly coloured blue and was as hard, bright and transparent as prior to colouring.

EXAMPLE 8

The colouring solution having the following constituents in admixture:

	by weight
sebacic acid	1.0%
ethylene glycol	28.0%
water	70.0%
brown dye consisting of a cellulose derivative (sold under the trade mark Sumikaron Brown S-SRL)	1.0%

was maintained at 57°C and a metal plate having a dry, clear lacquer coating was immersed therein for thirty seconds. The metal plate was removed from the colouring solution, washed in water and dried. It was found that the plate was uniformly coloured brown and the coating was as hard, bright and transparent as prior to colouring.

EXAMPLE 9

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	1.7%
azelaic acid	1.7%
ethylene glycol	27.0%
water	67.9%
blue dye (sold under the trade mark Sumikaron Blue SR)	1.7%

was maintained at 68°C and an exudative article made of an acrylic resin material was immersed therein for two months. After removing the article from the solution it was washed in water and dried. It was found that the article was uniformly coloured blue and was as hard, bright and transparent as prior to colouring.

EXAMPLE 10

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	2.6%
ethylene glycol	13.7%
1,3-propanediol	13.7%
water	68.3%
blue dye (sold under the trade mark Sumikaron Turquoise Blue S-GL)	1.7%

was maintained at 68°C and an exudative article made of an acrylate resin material was immersed therein for four minutes. After removing the article from the colouring solution, it was washed in water and dried. It was found that the article was uniformly coloured blue and was as hard, bright and transparent as prior to colouring.

EXAMPLE 11

A colouring solution having the following constituents in admixture:

	by weight
sebacic acid	2.5%
azelaic acid	3.3%
ethylene glycol	13.2%
1,3 - propanediol	13.2%
water	66.1%
blue dye (sold under the trade mark Kayalon Fast Blue FN)	1.7%

was maintained at 68°C and an exudative article made of an acrylate resin material was immersed therein for three minutes. After removing the article from the colouring solution, it was washed in water and dried. It was found that the article was uniformly coloured blue and was as hard, bright and transparent as prior to colouring.

Other synthetic resin materials, for example, polyurethane resin materials, polyamide resin materials, polycarbonate resin materials, acrylonitrile - butadiene - styrene copolymer resin materials and polyvinyl chloride resin materials may be coloured by the present invention. It is also possible to colour a film of dye the main component of which is a synthetic resin material. The colour tone is not limited by the type of synthetic resin material colour and synthetic resin materials may be coloured purple, orange, black etc. in addition to being coloured as in the Examples.

The present invention employs a coloured solution which includes at least one polyacid of the general formula:



i.e. a polyacid with a linear molecule with a carboxyl radical at each end. The polyacid may be adipic acid



pimelic acid



suberic acid



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azelaic acid



sebacic acid



5 dodecanedioic acid



Brasilic acid



tetradecanedioic acid

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15 Samples made in accordance with each of the above Examples were submitted to various tests, namely, a rubbing test with a sheet of cotton gauze and India rubber, a dipping test in artificial sweat consisting of a solution of three percent by weight of salt, and a soaping test. The colour tone of each sample was not effected by these tests. Other samples were left for six months and it was found that their colour was maintained without fading, change or the appearance of colour irregularities or spots.

20 The colouring solution used in the present invention contains 0.1% and 50% by weight of the polyacid. If the polyacid is present in an amount less than 0.1% by weight, the synthetic resin material is not coloured visibly and if it is present in an amount greater than 50% by weight, the surface of the synthetic resin material is liable to be damaged and, moreover, post-colouring treatment becomes rather difficult due to recrystallization of the polyacid. If n in the general formula of the polyacid is too low, an esterification reaction between the polyacid and the polyhydric alcohol is apt to start, and the colouring ability becomes weak and the life of the colouring is shortened.

40 The range of polyhydric alcohol in the colouring solution and which dissolves the polyacid is between 5% and 60% by weight. It is difficult to dissolve the polyacid in less than 5% by weight of the polyhydric alcohol and the colouring reaction is disturbed in more than 60% by weight polyhydric alcohol. 45 The polyhydric alcohol is preferably dihydric alcohol, for example, ethylene glycol



1,3-propanediol

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1,4-butanediol



1,5-pentanediol



and 1,6-hexanediol

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the general formula of the dihydric alcohol being:



Alternatively the polyhydric alcohol may be a trihydric alcohol, for example, glycerin

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From a practical point of view it is preferred that the polyhydric alcohol is a dihydric alcohol. In the case of a dihydric alcohol having the general formula:

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if N is too high, it is difficult to colour the synthetic resin. A monohydric alcohol is unsuitable for practical purposes because of the surface of the synthetic resin material is apt to be damaged.

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There is no limitation to the quantity of dye which may be included in the colouring solution, but its range is generally from 1% to 3% by weight.

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The method according to the present invention enables the surface of a synthetic resin material to be easily coloured in a relatively short time without damage and there is no necessity for additional treatment steps other than washing and drying. It is possible to colour synthetic resin material in nearly every colour, such as red, orange, yellow, green, blue, purple, brown and black except white, and there is no limitation of colour tone. The shade of colour is freely changeable by adjusting colouring conditions such as time of immersion in the colouring solution, temperature, composition of the colouring solution, and quantity of dye. Since the dye attaches only onto the surface of the synthetic resin material and does not permeate into the synthetic resin material, the surface of the synthetic resin material is not dissolved and the properties of the synthetic resin material are not effected.

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The external appearance of the synthetic resin material coloured by the present invention is not distinguishable from that of synthetic resin material in which dye is mixed by the conventional method.

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It is also possible to colour a synthetic

resin material by the present invention in such a way that partial colouring or graduation colouring or a pattern is produced. Even if after keeping a synthetic resin material coloured by the present invention for a relatively long time, it has been found that the colour condition has not deteriorated and is not removed by washing or rubbing. Since no chemicals having a poisonous character and no organic solvents are used in the present invention, there is no need to employ special techniques such as draining and exhaustion and there is no danger of pollution of the environment.

It will be appreciated that the present invention may be employed by continuously operating automatic equipment.

WHAT WE CLAIM IS:—

1. A method of colouring synthetic resin material comprising the steps of immersing the synthetic resin material in a colouring solution which is at a temperature less than the softening temperature of the synthetic resin material, the colouring solution comprising, in admixture, 0.1% to 50% by weight of at least one polyacid having a general formula:



where n is an integer between 3 and 15, 5% to 60% by weight of at least one polyhydric alcohol, a dye, and water.

2. A method as claimed in claim 1 in which the or each polyacid is one of adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, Brasilic and tetradecanedioic acid.

3. A method as claimed in claim 1 or 2 in

which the at least one polyhydric alcohol is a dihydric alcohol.

4. A method as claimed in claim 3 in which the or each dihydric alcohol is one of ethylene glycol, propanediol, butanediol, pentanediol and hexanediol.

5. A method as claimed in claim 1 or 2 in which the at least one polyhydric alcohol is a trihydric alcohol.

6. A method as claimed in claim 5 in which the trihydric alcohol is glycerin.

7. A method as claimed in any preceding claim in which the synthetic resin material is immersed in the colouring solution, which is at a temperature between 50°C and 95°C, for less than 5 minutes.

8. A method as claimed in any preceding claim in which the colouring solution contains between 1% and 15% by weight of the at least one polyacid.

9. A method as claimed in any preceding claim in which the colouring solution contains between 25% and 30% by weight of the at least one polyhydric alcohol.

10. A method as claimed in any preceding claim in which the colouring solution contains between 1% and 3% by weight of dye.

11. A method of colouring synthetic resin material substantially as herein described with reference to the Examples.

12. Synthetic resin material when coloured by the method claimed in any preceding claim.

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resin material by the present invention in such a way that partial colouring or graduation colouring or a pattern is produced. Even if after keeping a synthetic resin material coloured by the present invention for a relatively long time, it has been found that the colour condition has not deteriorated and is not removed by washing or rubbing. Since no chemicals having a poisonous character and no organic solvents are used in the present invention, there is no need to employ special techniques such as draining and exhaustion and there is no danger of pollution of the environment.

It will be appreciated that the present invention may be employed by continuously operating automatic equipment.

WHAT WE CLAIM IS:—

1. A method of colouring synthetic resin material comprising the steps of immersing the synthetic resin material in a colouring solution which is at a temperature less than the softening temperature of the synthetic resin material, the colouring solution comprising, in admixture, 0.1% to 50% by weight of at least one polyacid having a general formula:



where n is an integer between 3 and 15, 5% to 60% by weight of at least one polyhydric alcohol, a dye, and water.

2. A method as claimed in claim 1 in which the or each polyacid is one of adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, Brasilic and tetradecanedioic acid.

3. A method as claimed in claim 1 or 2 in

which the at least one polyhydric alcohol is a dihydric alcohol.

4. A method as claimed in claim 3 in which the or each dihydric alcohol is one of ethylene glycol, propanediol, butanediol, pentanediol and hexanediol.

5. A method as claimed in claim 1 or 2 in which the at least one polyhydric alcohol is a trihydric alcohol.

6. A method as claimed in claim 5 in which the trihydric alcohol is glycerin.

7. A method as claimed in any preceding claim in which the synthetic resin material is immersed in the colouring solution, which is at a temperature between 50°C and 95°C, for less than 5 minutes.

8. A method as claimed in any preceding claim in which the colouring solution contains between 1% and 15% by weight of the at least one polyacid.

9. A method as claimed in any preceding claim in which the colouring solution contains between 25% and 30% by weight of the at least one polyhydric alcohol.

10. A method as claimed in any preceding claim in which the colouring solution contains between 1% and 3% by weight of dye.

11. A method of colouring synthetic resin material substantially as herein described with reference to the Examples.

12. Synthetic resin material when coloured by the method claimed in any preceding claim.

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