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SURFACE-MODIFIED APPLICATORS AND METHODS THEREFOR

The invention is directed to applicators such as brushes, sponge-like absorbent applicators, and the like which have been surface-modified, for example by treatment with ion-producing gas plasma to improve adherence, wettability and other desirable characteristics.

Various techniques for altering the surface characteristics of polymeric materials with a reactor gas in the presence of an electromagnetic field are known. For example, U.S. patent specification no. 4 072 769 teaches a technique for modifying the surface of shaped, polymeric materials using a reactor gas of N_2O, water vapour, and the vapour of an organic compound. Another such technique is disclosed in U.S. patent specification no. 4 508 781, wherein the surfaces of synthetic or natural polymers are fluorinated by treatment thereof with inorganic fluorides in a cold glow discharge reactor. U.S. patent specification no. 4 925 698 teaches the fluorination of polymeric materials used in the manufacture of contact lenses. U.S. patent specification no. 5 108 667 discloses the fluorination of polymeric lipstick moulds which ultimately yield lipsticks with improved surface properties. U.S. patent specifications nos. 5 200 172 and

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4 978 524 teach the fluorination of cosmetic products such as lipsticks which provides them with a uniform, high gloss finish.

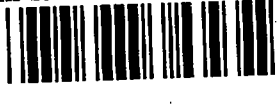
In general, the prior art techniques for plasma treatment have been limited to hard materials such as plastics, steel, iron and, more recently, cosmetics. However, we have hitherto had no knowledge of the surface treatment of applicators such as brushes, sponge-like applicators and the like. Further, it has most unexpectedly been discovered that plasma treatment of various applicators provides an applicator with improved hold, wettability, pickup, laydown, release and application.

The term "laydown" means the degree and ease with which an applicator releases its load of substance to be applied.

The term "pickup" means the degree to which an applicator is able to take up the substance to be applied when it is dipped into the substance or scraped or rubbed against the substance.

The term "application" means the way in which an applicator applies the substance to a surface. It is most desirable to have very smooth, even application without the clumping or streaking which is characteristic of natural fibre applicators. However, synthetic applicators

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generally do not provide a smooth, even application of the substance.

The invention provides an applicator suitable for applying a substance to a substrate, which applicator has a surface having a first wetting angle and a first surface area, which surface has grafted thereto a layer whose surface has a second wetting angle and a second surface area, wherein the second wetting angle is less than the first wetting angle and the second surface area is greater than the first surface area.

The invention also provides a method for simultaneously decreasing the wetting angle and increasing the surface area of an applicator surface which method comprises grafting to said applicator surface a layer whose surface has a wetting angle which is less than the wetting angle of the applicator surface, and a surface area which is greater than the surface area of the applicator surface.

The term "applicator" means a device or object suitable for applying a substance such as paint, polish, powder, make-up, nail enamel or the like to a surface. Included within this definition are objects such as paint rollers, buffing materials (eg imitation-chamois leathers used to polish cars, silverware polishing cloths, etc.), so-called 'sponges' such as cosmetic sponges, pads, so-called 'foams' such as foam wicks, powder puffs and

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brushes of all types (cosmetic brushes, nail enamel brushes, mascara brushes, industrial paint brushes). In the case of brushes, their so-called 'bristles' may be made of natural hair such as goat, pig, dog or horse hair, or they may be made of a synthetics material such as a plastics, nylon, or the like. The term "applicator" refers to the situation where the fibres are treated prior to their manufacture into applicators.

The term "layer" means a layer which is capable of becoming grafted (or chemically bonded) to the applicator surface. The layer may be bonded to the applicator surface by treatment of the applicator surface with an ion-producing gas plasma. The treatment may be carried out in an evacuative chemical vapour deposition chamber in accordance with any of the methods known in the art, for example any of the methods disclosed in U.S. patent specifications nos. 4 508 781, 5 108 667, 5 200 172 and 4 978 524, all of which are hereby incorporated by reference. The layer can also be grafted to the applicator surface by other methods such as by treatment of the applicator surface with a halogen in the presence of ultraviolet radiation as disclosed in U.S. patent specification no. 4 593 050, which is also hereby incorporated by reference.

The term "ion-producing gas" means a gas which produces ions in the presence of ultraviolet radiation or

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in a chemical vapour deposition chamber in the presence of an electromagnetic field. Examples of such gases include fluorocompounds such as fluoroC_{1-10}alkyls, air, nitrogenous gases, helium (He), argon (Ar), nitrous oxide (N_2O), fluorosilicons, and mixtures thereof. The electromagnetic field may be created by cold-glow discharge or similar means.

The term "wetting angle" means the angle (or contact angle) which exists between a specific liquid and a specific solid surface. This measurement gives an indication of the relative values of the forces of adhesion and cohesion that result in interfacial tension. As used herein, this term also indicates the ability of a specific solid surface to be wet by a specific liquid under defined conditions. The smaller the wetting angle of a liquid to a surface, the greater the wettability of its surface by the specific liquid and vice versa. A goniometer apparatus is usually used to measure wetting angles according to processes well known to those skilled in the art.

The method of the present invention causes the applicator to have a decreased wetting angle and an increased surface area, relative to its pre-treatment state. Hence, preferably, the second wetting angle of the substrate in an applicator in accordance with the invention has a value which is decreased to 5-99%, preferably 20-75%

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when compared to the first wetting angle of the original applicator surface before treatment according to the invention. Generally the wetting angles of suitable applicators prior to treatment range from 100-200°. The treatment causes the wetting angle to decrease to about 1-99°. For example, the synthetic bristles of an industrial paintbrush may have a wetting angle of 42° prior to any surface modification treatment, meaning that each individual 'bristle' has a respective wetting angle close to 42° and together, collectively, the 'bristles' have a first wetting angle of approximately 42°. After treatment according to the method of the invention, the layer applied to the 'bristles' causes the wetting angle of the individual 'bristles' to decrease so that collectively they yield a second wetting angle of about 21°, i.e. the wetting angle has decreased to 50 percent of its original or pre-treatment value.

The increase in surface area of the applicator may be attributable, for example, to the fact that the gas plasma forms an uneven or 'bubbled' layer on the applicator surface which is referred to in the art as 'etching'. Preferably, the method of the invention yields an applicator having etched surfaces wherein the thickness of the grafted layer of the gas plasma on the surface ranges from 50-5000 Angstroms. For example, if a synthetic nylon

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industrial paintbrush is treated according to the invention, generally a 50-5000 Angstrom etched layer of the gas plasma becomes grafted to the 'bristle' surfaces. Grafting occurs because the gas plasma constituents chemically react with the 'bristle' surfaces depositing a layer which bonds to the 'bristle' surface.

The method and applicators of the invention have advantages. For example, brushes made from natural fibres such as goat, dog, or horse hair are the most desirable in terms of quality, pick-up, laydown and ease of application. But expense and problems with availability often make it economically unfeasible to use natural fibre brushes for mass market purposes. In addition, natural fibre brushes require sterilization prior to commercial use due to natural biological contaminants. Most unexpectedly, the plasma treatment method of the invention provides synthetic bristle brushes which exceed the results achieved with natural fibre and at considerably less expense. It has also been found that when the plasma treatment method of the invention is performed on foam applicators, the applicators are less prone to yellow and crack. Yellowing and cracking of foam is a common problem associated with foam applicators.

Although the method of the invention may be used with all types of applicators, the preferred embodiments are

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directed to cosmetic applicators such as mascara brushes, make-up brushes, foam make-up applicators and the like.

The following examples are for illustration only and a person skilled in the art will understand there are other ways of putting the present invention into effect.

Example 1

A series of disc-shaped cosmetic foam applicators comprised of a commercially-available polyurethane were treated in accordance with the method of this invention. The foam applicators were suspended from a nylon cord attached by non-metallic clips at opposite ends of a reaction chamber of a chemical vapour deposition system to form a string of applicators. A commercially-available gas plasma treatment chamber supplied by Branson International Plasma Corp. (Division of SmithKline, Philadelphia, PA, USA) was used to modify the surfaces of the foam applicators. The aforementioned vacuum chamber assembly, having the string of disc-shaped foam applicators suspended within, was incorporated into an evacuative chemical vapour system used in known cold glow discharge polymerisation processes, and the fluorination process was carried out as follows:

The string of suspended foam applicators positioned within the vacuum chamber were treated with a gas containing about 5 percent by volume of tetrafluoromethane

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(CF_4) in a mixture of nitrous oxide (N_2O) and air. The gas was introduced into the vacuum chamber. Because of the porosity of the foam applicator surface, a mixture of N_2O and air, instead of helium, was used as a carrier gas to ensure complete fluorination. Initially, the vacuum pressure was gradually adjusted to a level of 50 microns or less and thereafter adjusted to a level not in excess of 5 microns. The contents of the vacuum chamber were then flushed with helium gas which was introduced at an increased level of from about 200 to about 1000 microns. After about five minutes, the vacuum chamber was re-evacuated to a pressure of from about 5 to about 50 microns. The fluorinated gas was then introduced into the vacuum chamber and maintained therein for a period of between 30 seconds and 15 minutes so as to allow complete saturation throughout the surface of the foam applicators. Upon completion of the CF_4 saturation, a cold glow discharge was generated throughout the vacuum chamber by means of direct electrical excitation at a power level of between about 50 to about 400 watts, thus initiating the chemical reaction of the plasma with the surfaces of the foam applicators. The plasma gas treatment was carried out from about 5 to about 6 minutes. Thereafter, the pressure within the vacuum was re-adjusted to ambient conditions, and the foam applicators were removed from the vacuum

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chamber. The treated products displayed undistorted sponge-like surfaces.

Subsequent testing of the foam applicators indicated that the surfaces had been fluorinated to a thickness of between 500 and 2000 Angstroms and that their respective wetting angles had been decreased from about 120-130 to about 70-80 degrees. The foregoing results were determined by means of a conventional electron spectroscopy for chemical analysis and a goniometer, respectively.

Example 2

The procedural steps outlined in Example 1 were repeated, except the respective surfaces of a series of synthetic foam wicks were modified in accordance with this invention. CF_4 was similarly used as the halogenating compound throughout the series along with a mixture of N_2O and air as the carrier gas during the gas plasma treatment. Helium was used to flush the reactor chamber before and after the halogenation procedure.

Upon being subjected to a relative absorbency and buoyancy test, the modified foam applicators exhibited a significant increase in absorbency. The aforementioned test involves placing a modified foam applicator along with a control (untreated) foam applicator into a container of water. The increase in absorbency of the treated foam applicator was evidenced by the fact that it sunk to the

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bottom of the container. In contrast, the control applicator continued to float on the water surface.

Based on visual inspection and the test results as described above, the surface characteristics of the treated foam wicks of this example were comparable to those obtained in Example 1.

Example 3

The following applicators were treated according to the invention:

12 nylon brushes

15 mascara brushes

12 nail brushes

Duplicate samples of all the above were retained, untreated, for comparison as controls.

The clean applicators were placed in a non-metallic holder, 20-25 pieces at a time. The holder was either a plastic or paper box or a plastic tube. The holders were then placed into a gas plasma treatment chamber (Branson International Plasma Corp., Division of SmithKline, Philadelphia, PA, USA). The vacuum was turned on to 0.1T for one hour to rid the chamber of all gases. After one hour of vacuum, the treatment gas was purged through the chamber for one minute while the vacuum was adjusted to 0.5T. The gas comprised about 5% by volume of CF_4, nitrogen, air or N_2O or mixtures thereof. The RF generator

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power switch was turned on until the power level reached 50-200 watts. After the gas plasma started, the vacuum was readjusted to 0.5T and the run was timed for 15-30 minutes. The vacuum was occasionally readjusted to 0.5T during the run. After 30 minutes, the gas, power and vacuum were turned off. The chamber was flushed with nitrogen gas to break the vacuum by turning on the purge switch. The chamber pressure then returned to atmospheric pressure. The door was opened and the applicators were removed and stored in clean, sealed plastic bags.

Results

The applicators treated according to Example 3 were evaluated against the untreated controls. Nylon brushes were evaluated for pickup, laydown and general application of powder. as well as for similarity to natural fibre brushes such as goat hair. Mascara brushes were evaluated for the same characteristics using Revlon's Long and Lustrous mascara formulation. The results are as follows:

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Run	Gas	Applicator	Time/Watts/Torr	Results
1	CF_4	nylon brush	15/150/.5	pickup was better than control. Comparable to untreated goat hair brush. Best application
2	CF_4	nylon brush	15/100/1	pickup better than control and N_2O treated, not as good as run 1
3	N_2	nylon brush	30/50/.5	comparable to control for pickup. Sample has slightly more evenness on application
4	N_2O	nylon brush	15/150/.5	better than control
5	air	nylon brush	30/50/.5	comparable to control
6	N_2	nylon brush	15/50/.5	better than control; comparable to run 2
7	N_2	nylon brush	15/100/.5	better than control; comparable to run 6
8	N_2O	nylon brush	15/50/.5	better than control; not as good as run 4
9	N_2O	nylon brush	15/100/.5 30/11/.5	better than control; comparable to goat hair
10	N_2O	foam	15/100/.5	better than control; best application
11	N_2O	foam	15/75/.5	better than control; not as good as run 11
12	N_2O	nylon brush	15/100/.5	comparable to control

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13	N_2O	nylon brush	30/100/1	slightly different brush to control. Very even laydown, pickup comparable to control
14	*	mascara brush	16/150/-	overall slightly better than control
15	**	mascara brush	5/200/-	overall slightly better than control
16	***	mascara brush	15/150/- 1 hr. vac.	overall slightly better than control
17	****	mascara brush	15/150/- 1 hr. vac.	overall slightly better than control

* gas = 1 min. O_2 and 15 min. CF_4

** gas = 50/50 mixture CF_4/O_2

*** gas = 1 min. CF_4

**** gas = 1 min. NO_3

Thus, treated applicators showed significant improvement in laydown, pickup and application when compared to untreated controls. Moreover, treated nylon brushes exhibited performance similar to that of natural fibre brushes.

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CLAIMS

1. An applicator suitable for applying a substance to a substrate, which applicator has a surface having a first wetting angle and a first surface area, which surface has grafted thereto a layer whose surface has a second wetting angle and a second surface area, wherein the second wetting angle is less than the first wetting angle and the second surface area is greater than the first surface area.

2. An applicator according to claim 1 wherein the layer is of ion-producing gas plasma.

3. An applicator according to claim 1 or claim 2 wherein the second wetting angle is 5-99% less than the first wetting angle.

4. An applicator according to any preceding claim wherein the second surface area is 10-90% greater than the first surface area.

5. An applicator according to any preceding claim wherein the second wetting angle is 1-99°.

6. An applicator according to any preceding claim wherein the thickness of the grafted layer of ion-producing gas plasma is 50-5000 Angstroms.

7. An applicator according to any preceding claim wherein the ion-producing gas is selected from N_2, N_2O, He, Ar, air, fluoroC_{1-10}alkyls, fluorosilicons, or mixtures thereof.

8. An applicator according to any preceding claim which is a brush, 'foam', 'sponge', puff or cloth.

9. A method for simultaneously decreasing the wetting angle and increasing the surface area of an applicator surface which method comprises grafting to said applicator surface a layer whose surface has a wetting angle which is less than the wetting angle of the applicator surface, and a surface area which is greater than the surface area of

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the applicator surface, comprising grafting to the applicator surface a layer of ion-producing gas plasma.

10. A method according to claim 9 wherein the applicator surface is treated with a halogen in the presence of ultraviolet light or with an ion-producing gas in a chemical vapour deposition system in the presence of a magnetic field.

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