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(54) Process for modification of animal hair.

(57) A process for modifying animal hair or a product thereof, which process comprises placing animal hair or a product thereof between two electrodes facing each other, in a plasma generator, introducing a plasma-excitable gas into the plasma generator and applying a high voltage of high frequency between the electrodes at atmospheric pressure to subject the gas to plasma excitation to give rise to glow discharge between the electrodes.

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The present invention relates to a process for modifying animal hair or a product thereof by a plasma treatment at atmospheric pressure. The process of the present invention is very simple and enables the significant improvement of the dyeability and shrinkage in washing, of animal hair or a product thereof.

Each animal hair such as wool or the like is hair covering each animal body and has such features that it has softness, curl and a high water-retaining property and, when made into textile products, has a high space ratio and an excellent heat-retaining property. Hence, it is in wide use as clothes.

Each animal hair has, on the surface, flakes called "cuticle" as shown in Fig. 1 (1 is a cuticle). (This is a big feature of animal hair.) Since the surface of each cuticle 1 is highly hydrophobic, the dyeing of animal hair is said to proceed in such a manner that a dye enters into the hair gradually through each gap 2 between the cuticles and the hair is dyed. The high hydrophobicity of the surface of animal hair requires a high temperature and/or a long time in dyeing the hair. The dyeing of animal hair at high temperatures allows the resulting animal hair product to have impaired touch. Hence, a technique for dyeing at low temperatures has been hitherto sought.

For modification of animal hair, particularly wool, it was tried to subject wool to a plasma treatment in vacuum. This approach had problems. That is, (1) a complicated and expensive apparatus is necessary to obtain a vacuum, and (2) the removal of water present inside the wool (the wool inside is hydrophilic) is time-consuming and a long time is required to obtain a high vacuum. Thus, the above approach is disadvantageous economically and moreover has low workability.

Wool further has a problem of shrinkage in washing. Untreated wool or wool products cause shrinkage in washing, and the shrinkage reaches 30 % or more in the case of Viyella® (a wool product).

According to the present invention there is provided a very simple process enabling the significant improvements of the dyeability and shrinkage in washing, of animal hair or a product thereof (e.g. wool or a product thereof).

One of the present inventors previously proposed a process for plasma-treating the surface of a plastic film or a synthetic fiber to impart high hydrophilicity to said surface, which process comprises placing a plastic film or a synthetic fiber in a plasma generator and generating a plasma in the generator at atmospheric pressure by glow discharge to subject the surface of the plastic film or the synthetic fiber to plasma treatment (Japanese Patent Application No. 187215/1990 and USP 5124173). The present inventors made further study on the above process and completed the present process capable of modifying animal hair remarkably.

According to the present invention there is provided a process for modifying animal hair or a product thereof, which process comprises placing animal hair or a product thereof between two electrodes facing each other, in a plasma generator, introducing a plasma-excitable gas into the plasma generator and applying a high voltage of high frequency between the electrodes at atmospheric pressure to subject the gas to plasma excitation to give rise to glow discharge between the electrodes.

The present invention is described in detail below.

An example of the plasma generator used in the present invention is shown in Fig. 2. In the atmospheric pressure plasma generator of Fig. 2, a wool cloth 2 is placed between two electrodes 1 facing each other. Preferably, a dielectric substance 3 such as glass, ceramic, polyimide film or the like is placed on the upper and/or lower electrode in order to prevent spark discharge during plasma excitation. A plasma-excitable gas (e.g. a mixture of argon and helium) is introduced into the atmospheric pressure plasma generator through an inlet 4 to discharge the air inside the generator and then is discharged from an outlet 5. Then, a high voltage of high frequency (e.g. 3,000 Hz and 4,200 V) is applied between the electrodes to subject the introduced gas to plasma excitation to give rise to glow discharge for a given length of time, whereby the wool cloth 2 is modified.

While Fig. 2 is an example showing the principle of the atmospheric pressure plasma generator of the present invention, an apparatus enabling a semi-continuous or continuous operation may be used as necessary. Fig. 3 shows an example of the apparatus for semi-continuous operation. In this apparatus, a belt-shaped wool cloth is fed through a slit 6. When the atmosphere inside the apparatus is converted into a predetermined plasma-excitable gas, a shutter 7 is closed to prevent the outflow of the gas and the inflow of air, and glow discharge is initiated to conduct a plasma treatment. When the treatment is over, the shutter 7 is opened; the cloth is moved forward by the length of electrodes; the shutter 7 is reclosed and the same treatment is repeated. When the cloth is very thin, a continuous operation (a continuous treatment) is possible by, for example, narrowing the diameter of the slit 6 and keeping the plasma-excitable gas inside the apparatus, at a pressure higher than atmospheric pressure.

In the present invention, "plasma-excitable gas" refers to a gas which is plasma-excitable when it is placed between two electrodes facing each other in an atmospheric pressure plasma generator and when a high voltage of high frequency is applied between the electrodes. Such a plasma-excitable gas is

exemplified by argon, helium, neon, cryptone, xenon, nitrogen, CO_2, flon gases (e.g. CF_4) and mixtures thereof. The gas may be used in combination with a ketone, a lower hydrocarbon gas, or other organic compound gas of relatively low boiling point as necessary for stabilization of glow discharge, etc. as long as the effect of the present invention is not impaired.

In one embodiment of the present invention, the plasma-excitable gas contains preferably argon and/or helium, more preferably argon and helium. Particularly preferably, the plasma-excitable gas is a mixture of argon and helium wherein the proportions of argon and helium are 80-10 parts by volume and 20-90 parts by volume, preferably 70-30 parts by volume and 30-70 parts by volume.

In another embodiment of the present invention, the plasma-excitable gas contains preferably argon and/or helium and a ketone, more preferably argon and a ketone. Particularly preferably, the plasma-excitable gas is a mixture of argon and a ketone wherein the proportions of argon and the ketone are 99.99-95 parts by volume and 0.01-5 parts by volume, preferably 99.9-99 parts by volume and 0.1-1 part by volume.

The ketone as a component of the plasma-excitable gas used in the present invention is preferably selected from the group consisting of acetone, methyl ethyl ketone and methyl isobutyl ketone. Acetone is most preferable.

The high voltage of high frequency applied between two electrodes in the present invention to conduct plasma excitation at atmospheric pressure, is appropriately set depending upon, for example, the properties of animal hair or a product thereof to be treated. In general, a voltage of 1,000-8,000 V, preferably 1,000-5,000 V is used. The frequency of electric source used is 500-100,000 Hz, preferably 1,000-10,000 Hz.

The present invention resides in a process for modification of animal hair or its product. In the present specification, "animal" refers to hair-covered mammals such as sheep, goat, rabbit and the like. "Animal hair" can be exemplified by wool, hair of Angola rabbit and hair of Kashmir goat. "Animal hair product" includes not only products made of animal hairs alone but also products made of mixtures between animal hair and other fiber (e.g. synthetic fiber), and can be exemplified by a cloth, a woven cloth, a knitted goods, an unwoven cloth and a loose fiber.

According to the modification process of the present invention, the surface of animal hair is easily endowed with high hydrophilicity. Thereby, the degree of dye exhaustion in animal hair or product thereof is increased, and a shorter dyeing time and a lower dyeing temperature can be employed. Further, the shrinkage in washing, of animal hair or product thereof is improved significantly.

The present invention is described more specifically below by way of Examples.

Example 1

A tropical was subjected to complete fat removal in a Soxhlet's extractor using toluene and ethanol as an extraction solvent, followed by through washing with water and drying to prepare a sample cloth.

In a reaction vessel shown in Fig. 2, lower and upper electrodes each made of brass and having a diameter of 50 mm were placed; onto each of these electrodes was laminated, as a dielectric substance, a 100 μ-thick polyimide film larger than each electrode; a wool cloth (the above-prepared sample cloth) of 100 mm x 100 mm was placed on the polyimide film laminated onto the lower electrode; the distance between the electrodes was set at 20 mm; the air inside the reaction vessel was replaced by a mixed gas consisting of equal volumes of argon and helium.

When the air was completely replaced by the mixed gas, a high-frequency voltage of 3,000 Hz and 4,200 V was applied between the upper and lower electrodes, whereby glow discharge of reddish purple color was generated and the wool cloth was subjected to a plasma treatment.

The wool cloth was treated as above for 10, 30, 60 and 180 seconds to obtain four treated cloths. Onto each of the treated cloths was dropped 6 μl of distilled water, and there was measured a time in which the water began to infiltrate into each treated cloth. The results were as follows.

Untreated cloth:	Infiltration began in more than 3,600 seconds.
Cloth treated for 10 seconds:	Infiltration began in 1,800 seconds.
Cloth treated for 30 seconds:	Infiltration began in 150 seconds.
Cloth treated for 60 seconds:	Infiltration began in 10 seconds.
Cloth treated for 180 seconds:	Infiltration began in less than 1 second.

Water infiltration was quick in the wool cloths treated for 30 seconds or more. Thus, the sample wool (natural fiber) was endowed with high hydrophilicity by a plasma treatment at atmospheric pressure.

Example 2

The procedure of Example 1 was repeated with the exception that the mixed gas used in Example 1 was replaced by a mixed gas obtained by adding about 5 ppm of acetone to argon (this mixed gas consisted of about 99.7 parts by volume of argon and 0.3 part by volume of acetone). The results were as follows.

Untreated cloth:	Infiltration began in more than 3,600 seconds.
Cloth treated for 10 seconds:	Infiltration began in 2,400 seconds.
Cloth treated for 30 seconds:	Infiltration began in 2,000 seconds.
Cloth treated for 60 seconds:	Infiltration began in 900 seconds.
Cloth treated for 180 seconds:	Infiltration began in 60 seconds.

The treated wool cloths showed improvement in hydrophilicity as compared with the untreated wool cloth.

Example 3

Wool was placed in a Soxhlet's extractor and subjected to wool fat removal using toluene and ethanol. The resulting wool was placed between two electrodes in a reaction vessel shown in Fig. 2. The air inside the vessel was replaced by a mixed gas consisting of equal volumes of argon and helium. A voltage of 3,000 Hz and 3,000 V was applied between the two electrodes, whereby glow discharge was allowed to appear and the wool was subjected to a plasma treatment. The treatment was conducted for 30 seconds and the treated wool was taken out to obtain a sample (1).

The same fat-removed wool as above was subjected to the same procedure as above except that the air inside the vessel was replaced by a mixed gas consisting of 99.7 parts by volume of argon and 0.3 part by volume of acetone. Thereby, a sample (2) was obtained.

Each of the untreated sample (wool subjected to no plasma treatment), the sample (1) and the sample (2) was dyed in a dyeing bath of 60 °C to measure the dye uptake with the lapse of dyeing time. The results are shown in Table 1. Incidentally, the dye used was Brilliant Scarlet 3R, which was an acid dye of levelling type, and the dyeing bath was prepared by adding 0.1 mole, per liter of water of KH_2PO_4 and the same amount of Na_2HPO_4 (buffer) to control the bath pH at 4.5.

Table 1

Sample	Dye uptake				
	20 min	40 min	60 min	80 min	100 min
Untreated sample	1.1	1.8	2.4	2.8	3.2
Sample (1)	2.7	4.0	5.0	5.6	6.1
Sample (2)	1.5	2.4	3.1	3.6	4.2
Note: Each figure in Table 1 indicates [(moles of dye adhered onto wool)/(g of wool)] x 10^5.					

Since wool is hydrophobic at the surface as mentioned previously, a high temperature and a long time are required in order for a dye to reach the equilibrium dyeing of wool. The time of half dyeing for each of the untreated sample, the sample (1) and the sample (2) was determined from the dye uptake at equilibrium dyeing at 60 °C, as follows.

Using Brilliant Scarlet 3R and the same dyeing bath as used in the above measurement of dye uptake, the untreated sample, the sample (1) and the sample (2) were measured for time of half dyeing ($t_{1/2}$). Shortening of dyeing time brings about large merits in economy and workability. The results are shown in Table 2.

Table 2

Sample	$t_{1/2}$
Untreated sample	117 min
Sample (1)	35 min
Sample (2)	77 min
Notes: Dye = Brilliant Scarlet 3R Dyeing temperature = 60 °C	

The sample (1), which was subjected to an atmospheric pressure plasma treatment using a mixed gas consisting of equal volumes of argon and helium, was dyed in a shortest time. The sample (2), which was subjected to the same atmospheric pressure plasma treatment using a mixed gas consisting of argon and acetone, was dyed in a longer time. The dyeing time for the samples (1) and (2), as compared with that for the untreated sample, was improved significantly.

As is clear from the above tests, the present process increases dye uptake and decreases dyeing time. It is not necessary to increase dyeing temperature for higher efficiency. This low dyeing temperature is advantageous because it does not impair the touch of wool. These meritorious effects of the present process are epoch-making.

Example 4

Viyella® (a wool product) not subjected to shrink-resistant finish was cut to prepare six samples each of 100 mm x 100 mm.

The two samples were not treated and were used for comparison. The other four samples were each subjected to a plasma treatment as follows. A glass plate as dielectric substance of 180 mm x 240 mm x 1 mm (thickness) was laminated onto each of upper and lower electrodes of 150 mm x 200 mm placed in an atmospheric pressure plasma reaction vessel; the distance between the two electrodes was set at 8 mm; a wool cloth (one of the above four samples) was placed between the electrodes and subjected to a plasma treatment by atmospheric pressure glow discharge, wherein the composition of the gas used and the treating time were as follows.

Gas composition	Treating time	Resulting sample
Argon = 60 parts by volume Helium = 40 parts by volume	30 seconds	1
Same as above	90 seconds	2
Argon = 99.7 parts by volume Acetone = 0.3 part by volume	30 seconds	3
Same as above	90 seconds Not treated	4 5 (for comparison)

The voltage applied was 3,000 Hz and 3,000 V.

Each of samples 1-4 (all treated) and sample 5 (not treated) was subjected to 20 times of washing (by an electric washing machine) and drying in accordance with JIS L-0127-103. Then, the dimension of each sample was compared with the dimension before washing, to determine the shrinkage percentage of each sample. The results are shown in Table 3.

Table 3

Sample	Shrinkage, %	
	Warp shrinkage	Filling shrinkage
1	18.4	14.0
2	13.1	18.2
3	18.2	27.4
4	10.6	6.6
5	39.4	32.7

Improvement in shrinkage percentage was large in samples 1-4. Unlike in the case of the dyeing test, the argon-acetone mixed gas gave a better result than the argon-helium mixed gas.

Example 5

The same wool fiber as used in Example 3 was placed between two Electrodes in an atmospheric pressure plasma reaction vessel shown in Fig. 1 (?); in this reaction vessel, glow discharge was allowed to appear between the electrodes by applying a high voltage of high frequency (1,000 Hz and 3,400 V) in a mixed gas consisting of 40 parts by volume of argon and 60 parts by volume of helium; thereby, the wool fiber was subjected to a plasma treatment. The resulting wool fiber was put in an acidic dyeing bath of 60 °C and the dyed fiber was compared with the untreated fiber. Incidentally, the acidic dyeing bath was prepared by using a milling dye (Kayanol Cyanine Blue 6B manufactured by Nippon Kayaku Co., Ltd.) and controlling the bath pH at 5.5.

The dye uptake, i.e. [(moles of dye adhered onto fiber)/(g of fiber)] x 10^6 with the lapse of dyeing time was as shown in Table 4.

Table 4

Sample	Dye uptake			
	12 hr	24 hr	36 hr	48 hr
Untreated	3.9	5.2	6.1	6.5
Treated	6.4	9.2	12.0	14.4

The time of half dyeing ($t_{1/2}$) was 22,245 min in the case of the untreated wool fiber and 9,057 min in the case of the treated sample. Thus, the dyeing time of the treated sample was less than half of that of the untreated sample.

Example 6

The same dyeing test as in Example 5 was conducted using Orange II which was an acid dye of levelling type. The dyeing bath pH was 4.5. In the plasma treatment, a mixed gas consisting of 99.5 parts by volume of argon and 0.5 part by volume of acetone was used; a voltage of 5,000 Hz and 2,600 V was applied; the other conditions were the same as in Example 1. The dye uptake, i.e. [(moles of dye adhered onto fiber)/(g of fiber)] x 10^6 with the lapse of dyeing time was as shown in Table 5.

Table 5

Sample	Dye uptake				
	10 min	20 min	30 min	40 mi	50 min
Untreated	3.4	4.9	6.2	7.0	7.2
Treated	5.5	7.5	9.0	10.0	10.0

The time of half dyeing was 42 min in the case of the untreated wool fiber and 18 min in the case of the treated wool fiber. Thus, also in Example 6, the dyeing time of the treated sample was less than half of that of the untreated sample.

Example 7

A tropical not subjected to shrink-resistant finish was cut to prepare six samples of the same size as in Example 4. Each of them was subjected to a plasma treatment using the same apparatus as in Example 4, to prepare the following samples 1-5.

Gas composition	Treating time	Resulting sample
Argon = 50 parts by volume Helium = 50 parts by volume	60 seconds	1
Same as above	180 seconds	2
Argon = 99.8 parts by volume Acetone = 0.2 part by volume	60 seconds	3
Same as above	180 seconds Not treated	4 5 (for comparison)

The voltage applied was 3,000 Hz and 3,300 V. The treating time was 30 seconds for the back side of each sample and 90 seconds for the front side.

Each of samples 1-4 (all treated) and sample 5 (not treated) was subjected to 20 times of washing by an electric washing machine to measure the shrinkage percentage of each sample. The results are shown in Table 6.

Table 6

Sample	Shrinkage, %	
	Warp shrinkage	Filling shrinkage
1	11.0	2.0
2	9.1	1.0
3	9.3	0.8
4	6.8	0.5
5	14.1	2.5

Shrinkage in washing was improved by a plasma treatment, also in the case of tropical. An argon-acetone mixed gas gave a better result than an argon-helium mixed gas,also in this Example.

Claims

1. A process for modifying animal hair or a product thereof, which process comprises placing animal hair or a product thereof between two electrodes facing each other, in a plasma generator, introducing a plasma-excitable gas into the plasma generator and applying a high voltage of high frequency between the electrodes at atmospheric pressure to subject the gas to plasma excitation to give rise to glow discharge between the electrodes.

2. The process set forth in Claim 1, wherein the plasma-excitable gas contains argon, helium or a mixture of argon and helium.

3. The process set forth in Claim 2, wherein the plasma-excitable gas contains a mixture of argon and helium.

4. The process set forth in Claim 3, wherein the proportions of argon and helium are 80-10 parts by volume and 20-90 parts by volume, respectively.

5. The process set forth in Claim 1, wherein the plasma-excitable gas contains a mixture of argon and a ketone, a mixture of helium and a ketone, or a mixture of argon, helium and a ketone.

6. The process set forth in Claim 5, wherein the plasma-excitable gas contains a mixture of argon and a ketone.

7. The process set forth in Claim 6, wherein the proportions of argon and a ketone are 99.99-95 parts by volume and 0.01-5 parts by volume, respectively.

8. The process set forth in any of Claims 5-7, wherein the ketone is selected from the group consisting of acetone, methyl ethyl ketone and methyl isobutyl ketone.

9. The process set forth in any of Claims 1-8, wherein the animal hair is wool.

FIG. 1

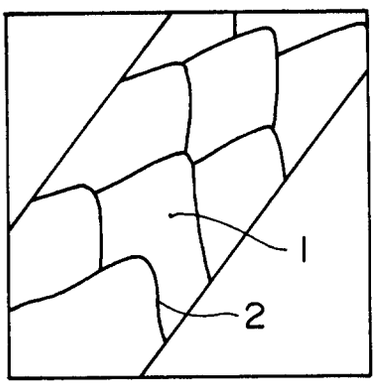

1
2

FIG. 2

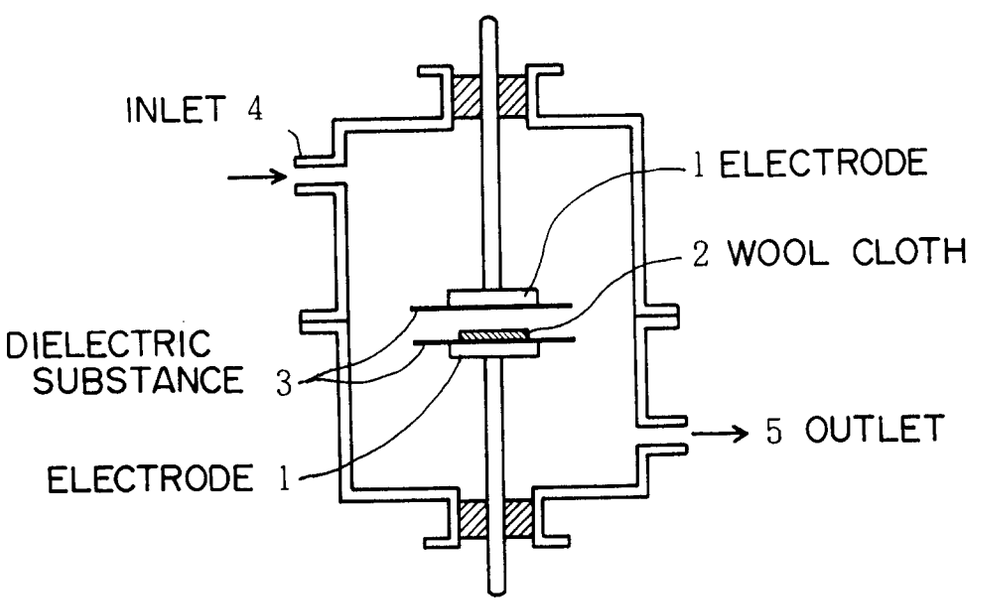
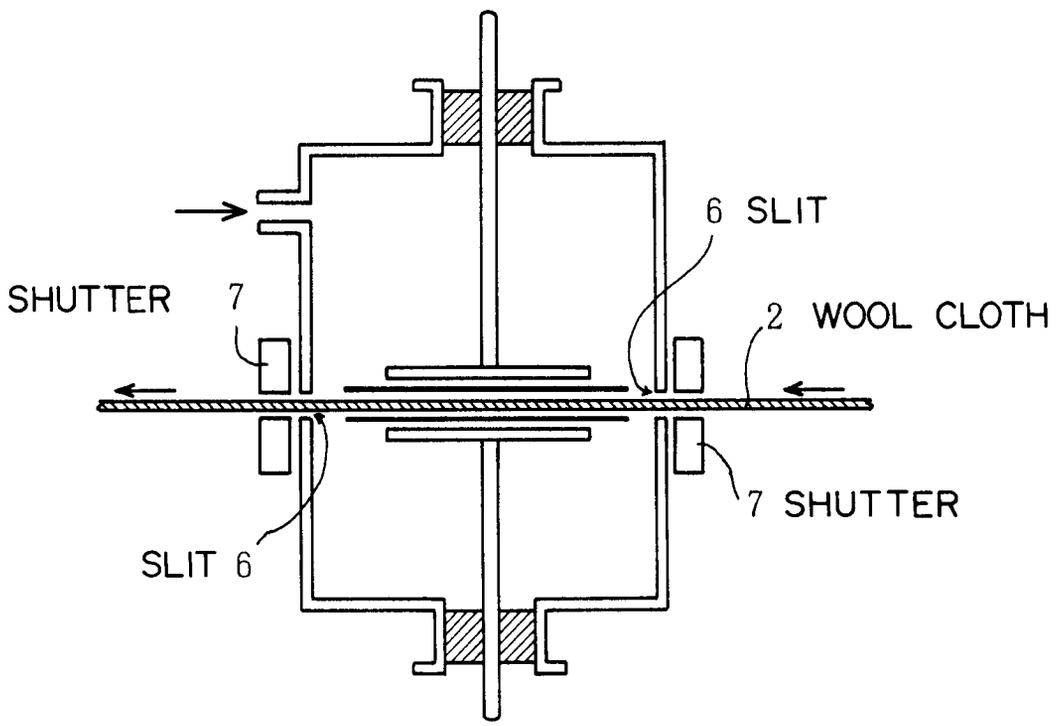

INLET 4
1 ELECTRODE
2 WOOL CLOTH
DIELECTRIC SUBSTANCE 3
5 OUTLET
ELECTRODE 1

FIG. 3



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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 6409

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y D	EP-A-0 467 639 (E.C. CHEMICAL CO. LTD.) * the whole document * & US-A-5 124 173 (UCHIYAMA HIROSHI ET AL.)	1-8	D06M10/02 D06P5/20
Y	HOLLAHAN J.R. ET AL. 'Techniques and applications of plasma chemistry' 1974 , WILEY INTERSCIENCE , NEW-YORK; USA Chapter 4, page 149-175, ATTILA E. PAVLATH 'Plasma Treatment of Natural Materials' * page 161 - page 170 *	1-8	
P,A	EP-A-0 548 013 (CIBA-GEIGY AG) * the whole document *	1-8	
A	US-A-3 632 299 (WALTER J. THORSEN) * claims *	1-8	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

D06M
D06P
B29C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 December 1993	Blas, V

CATEGORY OF CITED DOCUMENTS

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