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54 **A stain blocking system.**

57 A process for improving the stain resistance of polyamide and keratinous fibres and textiles is disclosed which comprises treating the fibres or textile in an aqueous dye bath at a long liquor ratio firstly with a fluorocarbon composition and subsequently with a stain blocker.

Description

A STAIN BLOCKING SYSTEM

This invention relates to a process for treating fibrous materials and textiles and in particular relates to a process for treating fibres and textiles in order to improve the stain resistance thereof.

Home furnishing textiles, in particular carpets, are subject to staining in use and it is inconvenient to subject them to frequent cleaning operations. Nylon carpets, for example, may be treated with compounds known as stain-blockers and/or fluorocarbons in order to increase their resistance to staining. One commonly employed treatment method, which fits in with the finishing routes employed on nylon carpets, is to treat the fibres with a stain blocker in a dye bath and subsequently spray fluorocarbon on to the finished carpet. One deficiency with this approach is that staining liquids often penetrate to the back of the carpet. After initial cleaning the immediately affected area on the top of the carpet pile is cleaned of stain, but the stain in the backing tends to wick up the pile producing staining around the original area. Furthermore, the methods of application used in connection with nylon carpet may not be applicable to home furnishings made of other fibres such as keratinous fibres like wool. Another deficiency with many existing treatments is the limited fastness of the treatment to shampooing and wear.

An object of the invention is to provide a process for applying stain blockers and fluorocarbons to keratinous and polyamide fibres.

Further objects and advantages of the invention will become apparent from the following description which is given by way of example only.

According to a broadest aspect of the present invention there is provided a process for improving the stain resistance of polyamide and keratinous fibres and textiles which comprises treating the fibres or textile in an aqueous dye bath at a long liquor ratio firstly with a fluorocarbon composition and subsequently with a stain blocker.

The invention further provides processes for improving the wet-fastness and durability of the stainblocking effect produced.

The joint use of a stain blocker and a fluorocarbon has been found by the applicants to be the preferred approach since while the stain blocker increases the resistance of the fibre to staining (with liquid colourants) it can actually have a detrimental effect on soiling, and the use of an effective repellent/soil resistant finish such as provided by a fluorocarbon is essential to give an overall effect which both improves the resistance of the textile to staining without lowering its resistance to soiling. Since the fluorocarbon provides a polymer coating to the fibre it would be expected that it should be applied subsequently to the stain blocker, or at least simultaneously in order not to impede uptake of the latter. It has been surprisingly found that much superior results are obtained in accordance with the invention by applying the fluorocarbon first and allowing it to exhaust on to the fibre before applying the stain blocker in the same bath. The applicants have found that a simultaneous application results in interference between the fluorocarbon and the stain blocker, incomplete exhaustion, and therefore poor results. Also, application of fluorocarbon subsequently to the stain blocker in the same bath does not give as good results as the process of the invention.

While the effectiveness of the invention in no way depends on the theory, it is believed that the stain blocker does not exhaust completely and residual stain blocker in the bath interferes with the application of the fluorocarbon. In the case of a fresh bath being used for fluorocarbon application, stainblocker on the fibre surface is believed to interfere with fluorocarbon application.

The process of the invention is particularly beneficial with wool fibres and textiles especially wool home furnishing textiles. The process can be applied at the loose wool, roving, slubbing, yarn, or made up textile article stages. Advantageously the process is applied in the dye bath immediately subsequent to dyeing or bleaching of the fibres.

The stain blockers which can be employed in the process of the invention are those currently available for this purpose, such as those described in European patent applications numbers 0242495 and 0242496. Such compounds are commercially available, inter alia, under the trade names Granofin WG (Hoechst AG), Mesitol NBS (Bayer), Alguard WR (Allied Colloids), Erionall RF (Ciba Geigy); or Scotchguard FX 369 (3M Corporation). Additionally, commercial compounds sold as synthetic tanning agents have been found to be effective, for example Baykanol HLX (Bayer) and Tanigan OS (Bayer).

Typical stain blockers are sulphonated phenol-formaldehyde or naphthol-formaldehyde condensation products. By sulphonated is meant that the product contains a $-SO_3H$ group or a salt thereof, such as an alkali metal salt.

The fluorocarbons useful in the process of the invention can be selected from those commonly used for textile treatments with the caveat that they should have good soil repellent characteristics and be compatible with subsequent application conditions so, for example, that they will not become de-exhausted under low pH conditions. Typical fluorocarbons useful in the invention comprise acrylate or urethane backbone chains with pendant fluorinated alkyl groups. Suitable fluorocarbons are available commercially under the trade names Teflon TC (DuPont), Scotchguard FC 397 (3M), Scotchguard FG 396 (3M) and Scotchguard FX 3602 (3M).

The process is advantageously carried out under acidic conditions, typically between pH 2 and 5, especially about pH 3, and the pH can be adjusted with sulphamic acid. The temperature is preferably elevated and can be in the region of 30 to 100 degrees Celsius, especially 50 to 80 degrees.

The process is an exhaustion process from long liquor ratios and liquor to goods ratios of 1:10 to 1:100 can be employed, typically a ratio of 1:30.

It has been found that the results of the process of the invention can be enhanced if certain other procedures are carried out in addition thereto. Firstly it has been found that, either a pre-treatment or preferably post-treatment with inorganic salts, in respect of the stain blocker, improves the performance of the treated fibre with regard to abrasion resistance and wet fastness. While it might be expected that the addition of different electrolytes would retard exhaustion (at low pH) it has been surprisingly found that certain zirconium and aluminium salts have an advantageous effect compared to other electrolytes. Not only was the stain resistance improved, but abrasion resistance and wet fastness of the treatment was enhanced.

A variety of auxiliaries can be added to the dye bath to promote exhaustion and/or distribution of the stain blocker. In general any effect seen was only marginal. However two particular auxiliaries, Baylan NT (Bayer) and Lanasan LT (Sandoz), used for the low temperature dyeing of wool, gave very significant improvements to the process.

Carpets are often steamed in a normal finishing route. However, it was unexpectedly found that atmospheric steaming of carpets treated in accordance with the process of the invention materially improved the stain blocking effect. Accordingly it is preferred to after treat carpets treated in accordance with the process of the invention with steam, e.g. for between 1 and 5 minutes, especially for about 2 minutes.

A particularly preferred carpet processing route is as follows:

Start at 20°C at long liquor ratio 1:20 to 1:60

Add 2% fluorochemical at pH 3 (sulphamic acid)

Raise to 50°C at 1 deg C/min. Run at 50°C for 30 min

Add 8% Stainblocker

2% Auxiliary

Readjust to pH 3-3.5 (sulphamic acid)

Raise to 65°C at 1 deg C/min. Run at 65°C for 30 min

Drop bath. Hydroextract and dry.

The above processing sequence is carried out in one bath, preferably in the dye bath subsequent to the dyeing operation.

If desired, the following fixing treatment can be employed as a pre- or post-treatment. In the case of a pre-treatment:

Start at 20°C at liquor ratio to 1:60

Add fixing chemical (low smoke Zirpro formulation (containing zirconium acetate) or $Al_2(SO_4)_3 \cdot 16H_2O$).

Raise to 70°C at 1 deg C/min. Run 30 minutes, and continue with the preferred processing route described above.

In the case of post-treatment: after running at 65° C for 30 minutes, add the fixing chemical. Run 15 minutes, then drop bath and rinse in cold water.

Hydroextract and dry.

After manufacture the carpet pile should preferably be steamed at atmospheric conditions for 2 minutes. Where carpet is of a tufted or cut pile construction it may be preferable to over spray the finished carpet with further fluorocarbon or stain blocker/fluorocarbon mixture to seal the cut ends and increase resistance to staining the improve durability of the stain resist treatment. With certain carpet treatments, for example carpets treated accordingly to the WRONZ CHEMSET method, the setting is sufficient to allow piece dyeing without significant loss of tuft definition. Since the process of the invention is applied after dyeing, the cut ends are treated in the exhaust bath obviating the need to over spray the carpet.

The invention will be illustrated further in the following examples.

EVALUATION METHODS

Assessment of resistance to abrasion

Fabric specimens are abraded against standard abrasive fabric using a Martindale Abrasion Tester for 500 rubs. The specimens were then stained.

Assessment of wet fastness properties

Detergent solution (10 ml/l of anionic detergent, pH 7.5 at 40°C) was applied under pressure and removed by vacuum using a spray extraction machine. This cleansing procedure was carried out five times. The dried specimens were then stained.

Staining method

Fabric specimens were individually agitated in a staining solution (0.8 g/l FD + C Red 40, 0.4 g/l citric acid, 0.1 g/l non-ionic wetting agent) at liquor to goods ratio of 20:1 for 5 min at 20°C. Excess solution was gently shaken off. Specimens were left to lie uncovered on a polyethylene sheet for 24 hours at ambient temperature, rinsed in cold water until no further stain was removed, hydro-extracted and dried for 30min at 60-70°C.

Measurement of stained wool

The colour difference, compared with untreated, was measured as ΔE (CMC) using an ICS Micromatch.

EXAMPLES

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Stainblocker Treatments on Wool

Example	Treatment	ΔE (24 hour stain)		
		after treatment	after cleaning	after abrasion
0	Untreated	30.2	32.2	36.3
1	10% SB, steamed	7.9	11.3	32.9
2	10% SB, 2% Baylan NT, steamed	2.3	3.0	31.1
3	3% FC, 8% SB, 2% Baylan NT, steamed	1.0	1.8	25.7
4	3% FC, 8% SB, 2% Baylan NT, not steamed	3.2	4.8	28.2
5	8% SB, 2% Baylan NT, pH 3.5, 3.5% K ₂ ZrF ₆ , 7.7% ZrAc, pH 2	1.5	2.3	22.9
6	8% SB, 2% Baylan NT, pH 3.5, 10% Al ₂ SO ₄	1.3	1.6	19.6
7	6.8 citric acid, 10% Al ₂ (SO ₄) ³ 16H ₂ O pH2, 8% Baylan NT, steamed	2.1	2.6	23.5

All fluorocarbon and stain blocker treatments were applied at pH 3 to 3.5, adjusted with sulphamic acid, at 65°C for 30 minutes. All concentrations are as supplied and on weight of wool. FC = fluorocarbon (Scotchguard FC 397) SB = stain blocker (Mesityl NBS)

Stainblocker Treatments on Nylon 6 and 66

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Example	Treatment	ΔE (24 hour)	
		nylon 6	nylon 66
7	Untreated	52.7	43.3
8	5% Mesityl NBS	3.9	3.3
9	5% Mesityl NBS, 2% Baylan NT	3.3	2.8
10	2% FC 397, 5% Mesityl NBS	4.8	4.5
10	2% FC 397, 5% Mesityl NBS, 2% Baylan NT	3.8	4.5

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Some test results on carpets are shown on the accompanying tables in which Figure 1 shows a durability trial using a hexapod carpet wear testing mechanism. The carpet samples were all stained with a solution of a food dye, Amaranth, 0.08 g/l by introducing 10ml of the dye solution onto the carpet surface using a standard

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stain applicator which evenly applies the dye solution over an 80 mm diameter circular area. This was left to dry for 24 h and removal of the stain was attempted using a commercial hot water extraction carpet shampooer with appropriate detergent. The carpet was then dried and the amount of residual stain remaining was measured by a Minolta Chroma-meter CR110 with the results calculated as colour difference (ΔE) with respect to the unstained carpet.

It can be seen that from Figure 1 Baykanol HLX treated carpet has good initial resistance to staining (ΔE of 2) but that after the carpet has undergone wear in the Hexapod the resistance to staining decreased (ΔE of 25 after 1000 revolutions) although it remains better than untreated carpet.

However, carpet treated with Baykanol HLX, Baylan NT and with an aluminium sulphate after treatment shows much better resistance to staining after wear (ΔE of 5 after 1000 revolutions).

Figure 2 shows results of staining carried out after various numbers of shampooing cycles. Baykanol HLX treated samples showed some loss of stain-resistance after shampooing; with Baylan NT as an auxiliary and an aluminium sulphate aftertreatment there is virtually no loss in stain-resistance after shampooing.

Thus by this invention there is provided a stain blocking process for fibrous materials and textiles. Particular examples of the invention have been described and it is envisaged that modifications can take place without departing from the scope of the appended claims.

Claims

1. A process for improving the stain resistance of polyamide and keratinous fibres and textiles comprising treating the fibres or textile in an aqueous dye bath at a long liquor ratio firstly with a fluorocarbon composition and subsequently with a stain blocker.
2. A process according to claim 1 further comprising processes for improving the wet-fastness and durability of the stain blocking effect produced.
3. A process according to claim 2 in which the wet-fastness and durability are improved by the joint use of a stain blocker and a fluorocarbon.
4. A process according to claim 3 in which the fluorocarbon is applied first and allowed to exhaust on to the fibre before applying the stain blocker in the same bath.
5. A process according to any preceding claim in which the fibres and textiles are wool fibres and textiles especially wool home furnishing textiles.
6. A process according to claim 5 in which the process is carried out at the loose wool, roving, slubbing, yarn, or made up textile article stages.
7. A process according to claim 6 in which the process is carried out in a dye bath immediately subsequent to dyeing or bleaching of the fibres.
8. A process according to any preceding claim in which the stain blocker is a phenol-formaldehyde or naphthol-formaldehyde condensation product containing a $-SO_3H$ group or a salt thereof, preferably an alkali metal salt thereof.
9. A process according to any preceding claim in which the stain blockers employed in the process are those described in European patent applications numbers 0242495 or 0242496 or the compounds commercially available, inter alia, under the trade names Granofin WG (Hoechst AG), Mesitol NBS (Bayer), Alguard WR (Allied Colloids), Erional RF (Ciba Geigy); and Scotchguard FX 369 (3M Corporation).
10. A process according to claim 8 in which synthetic tanning agents such as Baykanol HLX (Bayer) and Tanigan OS (Bayer) are used as stain blockers.
11. A process according to any preceding claim in which the fluorocarbon is a compound having an acrylate or urethane backbone with pendant fluorinated alkyl groups.
12. A process according to any preceding claim in which the fluorocarbons are those commercially available under the trade names Teflon TC (DuPont), Scotchguard FC 397 (3M), Scotchguard FG 396 (3M), and Scotchguard FX 3602 (3M).
13. A process according to any preceding claim in which the process is carried out under acidic conditions, preferably between pH 2 and 5, particularly preferably about pH 3.
14. A process according to claim 13 in which the pH is adjusted with sulphamic acid.
15. A process according to any preceding claim in which the temperature is in the region of 30 to 100 degrees Celsius, preferably 50 to 80 degrees Celsius.
16. A process according to any preceding claim in which the process is an exhaustion process from long liquor ratios and a liquor to goods ratio of 1:10 to 1:100, preferably 1:30, is employed.
17. A process according to any preceding claim in which a pre-treatment or post-treatment with inorganic salts, in respect of the stain blocker, is applied to improve the performance of the treated fibre with regard to abrasion resistance and wet fastness.

Figure 1: Durability to wear

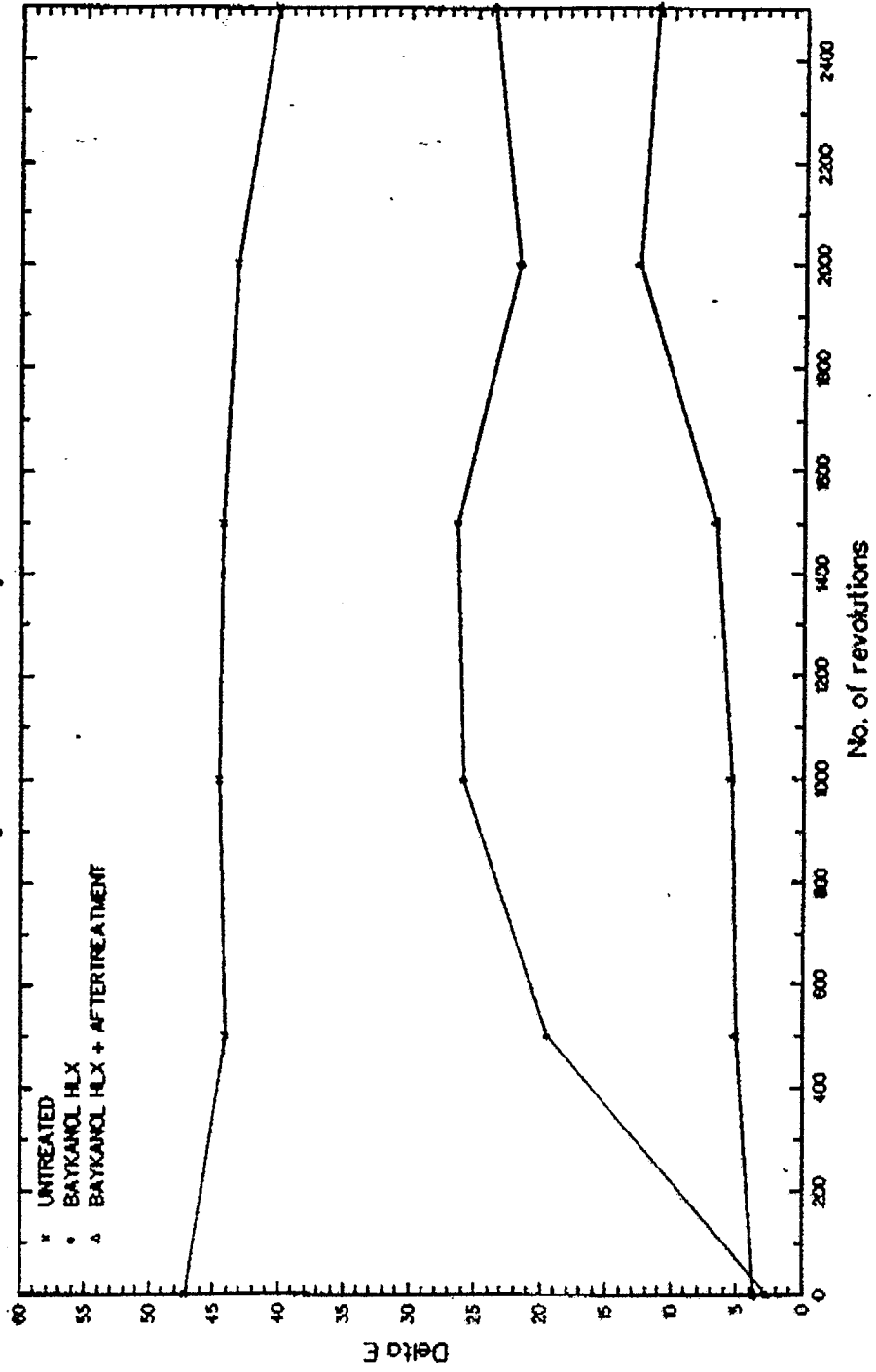
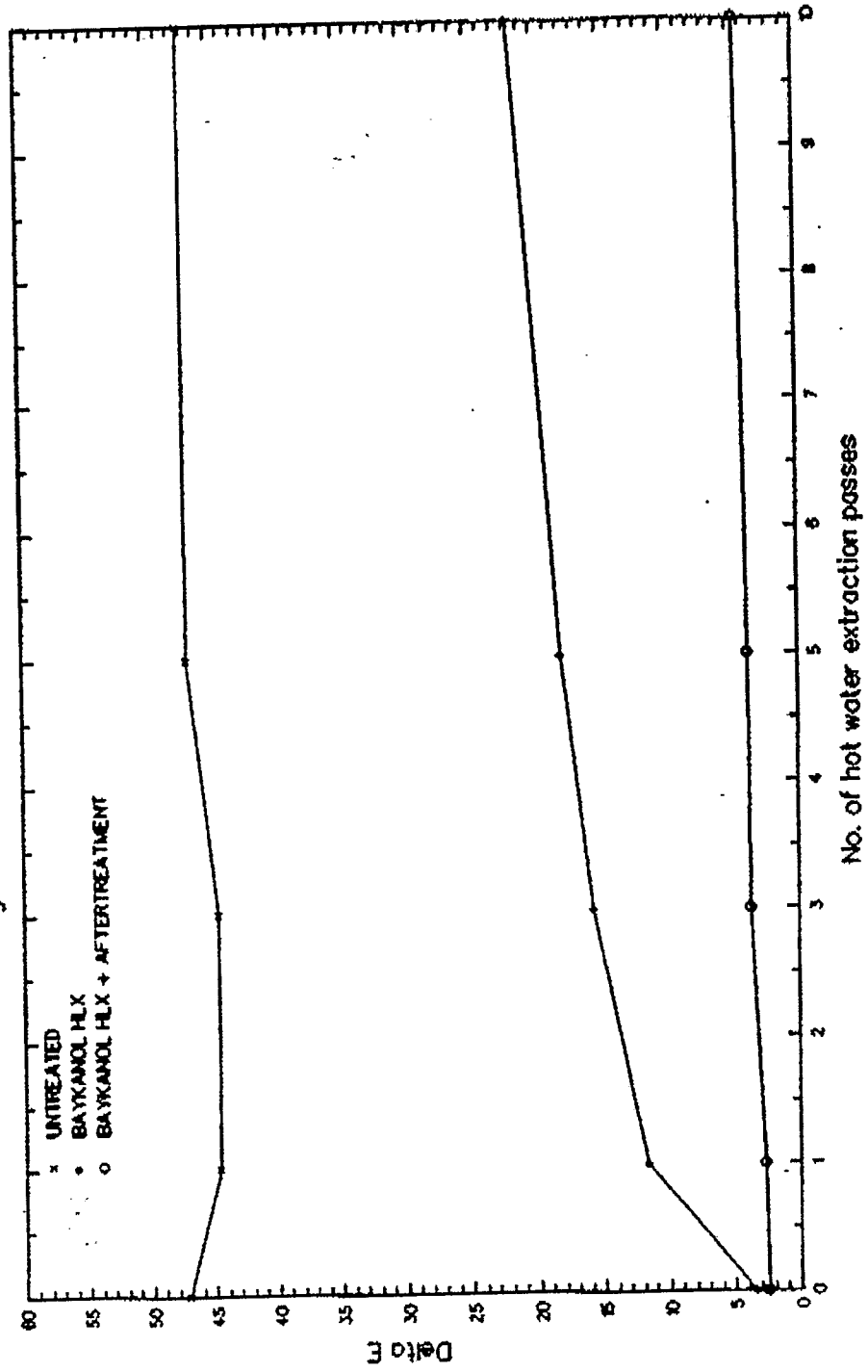


Figure 2: Fostrness to shampooing





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)
X	EP-A-0 242 496 (MONSANTO) * Abstract; page 3: "Summary"; page 5, lines 5-33 *	1-4	D 06 M 15/277 D 06 M 15/41
D	---	8-15	
X	WO-A-8 802 042 (ALLIED CORP.) * Abstract; page 2: "Summary"; page 2, line 15 - page 5, line 22; claim 1 *	1-4,8-10,15	
A	FR-A-2 277 927 (HCA MARTIN INC.) * Page 5, lines 2-29; page 6, lines 17-37; claims 1,3,4 *	1,8	
A	GB-A-1 165 203 (MINNESOTA MINING) * Page 1, lines 12-20; page 8, lines 16-25 *	1-4,8	
A	US-A-3 459 696 (READ et al.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 06 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-09-1989	Examiner DELZANT J-F.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			