

Clarke, Modet & C^o
COLOMBIA

ESCOBAR - URIBE ASOCIADOS
Intellectual Property

As. 3057/PCT.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACION
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 07-045770- -00002-0000

Fecha: 2008-05-22 08:56:13 Dep. 2020 NUECREACION
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 538 PETICION Folios: 5

Ref.: Expediente No. **07-045.770**
Solicitud de Patente a nombre de
HUNTSMAN ADVANCED MATERIALS (Switzerland GmbH)

Yo, **JIMENA ESCOBAR URIBE**, identificada como aparece al pie de mi firma, domiciliada en Bogotá, en la Carrera 11 No. 86-53, piso 6, obrando como apoderada de la sociedad **HUNTSMAN ADVANCED MATERIALS (Switzerland GmbH)**, con domicilio en Basilea, Suiza, solicitante de la patente de la referencia, pido a usted que se proceda a examinar si la invención, cuya patente se tramita en el expediente de la referencia, es patentable.

Adjunto al presente memorial el recibo No. 08-32,066 de 21 de abril de 2008, 08-33,842 de 25 de abril de 2008, 08-37,893 de 13 de mayo de 2008, 08-37,856 de 13 de mayo de 2008, por la suma de \$420.000.00, con lo cual queda cubierta la tasa oficial correspondiente a dicho estudio.

Señor Superintendente,


JIMENA ESCOBAR URIBE
C.C.39.779.452 de Usaquén
T.P.No. 68228
Còd.5376



RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

60

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-045770- -00002-0000

Fecha: 2008-05-22 08:56:13 Dep. 2020 NUECREACION
Tra. 11 PATENTEIYII Eve: 378 FASENACIONAL
Act. 538 PETICION Folios: 5

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 32,066
FECHA : ABRIL 21 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Gr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	136010	21/04/2008	23,492,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	54 INFORMACION DETALLADA DE UN TRAMI
			TOTAL :
			23,000.00
			23,000.00

SON: VEINTITRES MIL PESOS

2
3057.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-045770- -00002-0000

Fecha: 2008-05-22 08:56:13 Dep. 2020 NUECREACIONE
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 538 PETICION Folios: 5

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 08 - 33,842
FECHA : ABRIL 25 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693033	25/04/2008	33,000,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	21 CERTIFICACIONES
			11,000.00
		TOTAL :	\$ 11,000.00

SON: ONCE MIL PESOS

RESPONSABLE : _____

62

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-045770- -00002-0000

Fecha: 2008-05-22 08:56:13 Dep. 2020 NUECREACION
Tra. 11 PATENTE I Y II Eve: 378 FASE NACIONAL I
Act. 538 PETICION Folios: 5

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 08 - 37,893
FECHA : MAYO 13 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693044	13/05/2008	9,190,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	99 OTROS SERVICIOS ADMINISTRATIVOS
			TOTAL : \$ 120,000.00

CIENTO VEINTE MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

4

63

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-045770- -00002-0000

Fecha: 2008-05-22 08:56:13 Dep. 2020 NUECREACIONE
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 538 PETICION Folios: 5

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 900176089-2

RECIBO OFICIAL DE CAJA : 08 - 37,856
FECHA : MAYO 13 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO DE BOGOTA	062754387	693044	13/05/2008	9,190,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-04	PRESENTACION DE OBSERVACIONES	
		12 MARCAS Y LEMAS COMERCIALES	266,000.00
		TOTAL :	\$ 266,000.00

DOSCIENTOS SESENTA Y SEIS MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

5
41307

6A

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 07-45770

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **583** DE

FECHA **18 DE DICIEMBRE DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL **14 DE MARZO DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号

特開平8-27674

(43) 公開日 平成8年(1996)1月30日

(51) Int.Cl.⁶

D 0 6 M 15/55

識別記号

庁内整理番号

F I

技術表示箇所

審査請求 未請求 請求項の数 1 O L (全 8 頁)

(21) 出願番号

特願平6-162156

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平成6年(1994)7月14日

(71) 出願人 000004503

ユニチカ株式会社

兵庫県尼崎市東本町1丁目50番地

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三重県度会郡小俣町明野476-8

(72) 発明者 稲岡 美恵子

大阪府吹田市千里丘西16-22

(54) 【発明の名称】 天然ポリアミド系繊維の黄変防止加工方法

(57) 【要約】

【目的】 ウール、絹等の天然ポリアミド繊維の黄変を未然に防止する加工方法を提供する。

【構成】 ウール、絹等の天然ポリアミド繊維にセミカルバジド系化合物と多価アルコール系エポキシ化合物を含む処理液を付与し、乾熱処理を施す。

PAT-NO: JP408027674A
DOCUMENT-IDENTIFIER: JP 08027674 A
TITLE: METHOD FOR PROCESSING FOR
PREVENTING NATURAL POLYAMIDE-
BASED FIBER FROM YELLOWING
PUBN-DATE: January 30, 1996

INVENTOR-INFORMATION:

NAME	COUNTRY
NISHIMURA, TEIJIRO	
INAKA, MIEKO	

ASSIGNEE-INFORMATION:

NAME	COUNTRY
UNITIKA LTD	N/A

APPL-NO: JP06162156
APPL-DATE: July 14, 1994

INT-CL (IPC): D06M015/55

ABSTRACT:

PURPOSE: To prevent a natural polyamide-based fiber from yellowing by applying a treating liquid containing a specific compound to the fiber and then carrying out the dry heat treatment of the resultant fiber.

CONSTITUTION: This method for processing for

preventing a natural polyamide-based fiber from yellowing is to apply a treating liquid containing a semicarbazide-based compound and a polyhydric alcohol-based epoxy compound to the natural polyamide-based fiber such as wool or silk by a dipping, a padding method, etc., and then carry out the dry heat treatment (at 50-110°C). Thereby, preventing effects on yellowing having practical durability are imparted thereto without deteriorating the feeling unique to the fiber. Furthermore, compounds of formulas I to IV can be exemplified as the semicarbazide-based compound and compounds of formulas V to VII can be exemplified as the polyhydric alcohol-based epoxy compound.

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Disclaimer

This English translation is produced by machine translation and may contain errors. The JPO, the INPI, and those who do not are not liable for the result of the translation.

Notes

1. Unreadable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as is.

Translated: 06/30/2009 JST 07/01/2009

Priority: Last updated 06/08/2009 / Priority

CLAIM + DETAILED DESCRIPTION**[Claim(s)]**

[Claim 1]yellowing of a natural polyamide fiber giving a treating solution which contains a semi KARUBAJIDO system compound and a polyhydric alcohol system epoxy compound in a natural polyamide fiber, and carrying out dry heat treatment to after an appropriate time -- a prevention processing method.

[Detailed Description of the Invention]**[0001]**

[Industrial Application]This invention relates to the processing method which prevents beforehand yellowing of natural polyamide fibers, such as wool yarn and silk.

[0002]

[Description of the Prior Art]Since natural polyamide system animal-hairs textiles, such as wool yarn, are excellent in functionality, such as **** and moistness, garments are widely used for interior materials including the interior material of an airplane and a car, etc. from the first.

However, if these natural polyamide system animal-hairs textiles result in the natural polyamide system animal-hairs textiles which have the fault that the textiles themselves turn yellow easily with light or heat, and performed bleaching and dyeing, its fading and discoloration resulting from yellowing by light or heat are large, and they have been old pending questions.

[0003]as the method of cause of yellowing of natural polyamide system animal-hairs textiles and investigation of a mechanism being performed, and preventing yellowing especially by light the place by the present -- an ultraviolet ray absorbent and yellowing -- the method of giving a prevention agent to textiles is examined.

[0004]first -- since typical ultraviolet ray absorbents, such as a benzotriazole compound, a

benzophenone series compound, a hinder TOAMIN system compound, do not have a water-soluble machine, they are not absorbed by animal-hairs textiles -- the yellowing -- the prevention effect is not accepted at all. Recent years come, and according to the report of the 8th international wool research conference in 1994. benzo[the 2-hydroxy benzophenone which can introduce a sulfone group into these compounds and can stick to animal-hairs textiles as colorless acid dye and / 2-hydroxyphenyl] -- doria -- ZORU, 2-hydroxyphenyl S-triazine, etc. being developed and by using these. yellowing of textiles -- although the prevention effect came to be accepted, the effect of the level which a market requires is not reached.

[0005]receiving the silk fiber of a natural polyamide system on the other hand -- yellowing -- although a semi KARUBAJIDO system compound is effective as a prevention agent, it has the fault that it is scarce, in the endurance of the effect. Even if animal-hairs textiles are not adsorbed easily but this semi KARUBAJIDO system compound is adsorbed, it will drop out easily by wash and dry-cleaning processing, and practical use endurance will have a scarce fault.

[0006]Thus, the actual condition is that it is not yet established even if the practical processing method which prevents yellowing of natural polyamide fibers, such as animal-hairs textiles and a silk fiber, continues up to now.

[0007]

[Problem to be solved by the invention]yellowing where this invention was performed in view of such the present condition and which has practical use endurance in a natural polyamide fiber -- it aims at acquiring the processing method which gives prevention performance.

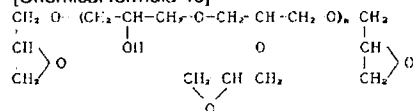
[0008]

[Means for solving problem]This invention has the next composition to achieve the above objects. namely, yellowing of a natural polyamide fiber, wherein this invention gives the treating solution which contains a semi KARUBAJIDO system compound and a polyhydric alcohol system epoxy compound in a natural polyamide fiber and carries out dry heat treatment to after an appropriate time -- let a prevention processing method be a gist. Hereafter, this invention method is explained in detail.

[0009]this invention -- a natural polyamide fiber -- yellowing -- it uses as an object of prevention processing. The nature textiles of a natural keratin and the nature textiles of a natural keratin which are obtained from animals, such as the sheep, cashmere, mohair, Angora, a camel, an alpaca, and a vicuna, silk, collagen textiles which have PEPUCHIDDO combination in a molecule similarly, etc. shall be meant as a natural polyamide fiber here. The form of the above-mentioned textiles may be a form of thread, knitting, textiles, a nonwoven fabric, a sewing article, etc. besides rose hair and a sliver, and the textiles themselves may be 100% of natural polyamide fibers, and it may be together used with other textiles in less than 85% of

[0022]

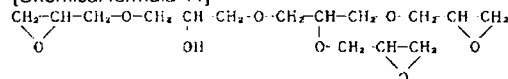
[Chemical formula 10]



(ただし、nは2または3)

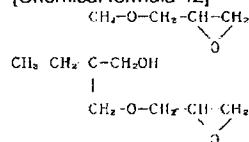
[0023]

[Chemical formula 11]



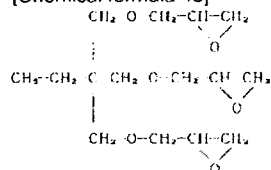
[0024]

[Chemical formula 12]



[0025]

[Chemical formula 13]



[0026] Although an above-mentioned polyhydric alcohol system epoxy compound is used in 0.1 to 3.0 weight % of the range to textiles, it is 0.5 to 2.0 weight % of a range preferably.

[0027] Although the treating solution containing an above-mentioned semi KARUBAJIDO system compound and polyhydric alcohol system epoxy compound is given to a natural polyamide fiber in this invention, as the grant method at this time, it can carry out by proper means, such as the immersing method, the pad method, and the spray method. When adopting the immersing method, after adjusting solution containing a with a semi KARUBAJIDO compound with a concentration of 2-60g/l. and a concentration of 10-150g/l. polyhydric alcohol system epoxy resin to normal temperature -50 °C and making it immersed

for 5 to 20 minutes, it deliquors and dries by ***** of 30 to 80% with a centrifugal dehydrator.

In adopting the pad method, solution containing a with the semi KARUBAJIDO compound of 5 to 100% of concentration and a concentration of 10-100g/l. polyhydric alcohol system epoxy resin is adjusted to normal temperature -50 °C like the immersing method, and it deliquors and dries by ***** of 50 to 100% with mangle after being impregnated.

[0028] then, yellowing which has practical use endurance by carrying out dry heat treatment of the processed textiles at the temperature of 50-110 °C in this invention method -- the natural polyamide fiber of this invention which has the prevention effect can be obtained.

[0029]

[Function] yellowing which was excellent in the semi KARUBAJIDO system compound itself, although it has the prevention performance, Since there is no functional group which can be combined among natural polyamide fibers, such as wool yarn, textiles are not adsorbed, but drop out easily by processing of wash, dry cleaning, etc., and turn yellow to the same extent as an unprocessed natural polyamide fiber, but. If a polyhydric alcohol system epoxy resin is used together to a semi KARUBAJIDO system compound and a natural polyamide fiber is processed like this invention, The epoxy group of a polyhydric alcohol system epoxy resin is an active group of a natural polyamide fiber. - It reacts to NH_2 , $-\text{COOH}$, $-\text{OH}$, $-\text{SH}$, etc. easily.

yellowing which adheres on textiles and has the practical use endurance over wash, dry-cleaning processing, etc. -- the natural polyamide fiber which has the prevention effect comes to be obtained.

[0030]

[Working example] Next, although the embodiment explained this invention method still more concretely, measurement of yellowing of the animal-hairs textiles in an embodiment and evaluation were performed by the following method.

[0031] (1) yellowing -- JIS L-0842, [a tightness °C fading resistance test method sample] glaring for 80 hours using a carbon arc ***** machine on with the arc currents (exchange) 15-17A, the arc voltage (exchange) 125-140V, and an inside the plane temperature of 63 °C conditions -- yellowing after irradiation -- the macro-scopic judging estimated the degree in the following four steps.

O : °C as which yellowing is not regarded: x which has turned yellow a little : xx which has turned yellow : It has turned yellow very much. [0032] °C After performing the irradiation by the fading resistance test method of a ***** method above-mentioned °C paragraph, spectrum reflectance was measured using the Macbeth MS-2020 type **** machine, and the color difference of the CIEL * a * b * color system estimated.

[0033] °C After the nitric oxide gas examining method sample is immersed in the alcoholic liquid of 1% of butyl hydroxyl toluene concentration, make alcohol evaporate and, subsequently using a nitric oxide gas fastness test machine with phosphoric acid and nitrous acid. the

sample immediately after generating about 500 ppm nitric oxide gas, and processing in 30 ** atmosphere for 2 hours, and this yellowing -- using the sample after an examination as foundation cloth -- yellowing -- the same sample that is not examining being used as an attachment cloth, and. [the sample] It piled up on it and the macro-scopic judging estimated the both sides of the foundation cloth after neglect, and an attachment cloth for seven days in the following four steps.

O : ** as which yellowing is not regarded: x which has turned yellow a little : xx which has turned yellow : It has turned yellow very much. [0034](2) Practical use durability test ** It processes for 10 minutes at normal temperature by the perchlorethylene containing dry cleaning detergent of the dry-cleaning ** ratio 1:8, and is considered as one dry cleaning, and this is repeated 10 times.

[0035]** Rub, by washing washing method JIS L-0217 (the 106 methods), fold up a sample in 30 ** of solution temperature, and 2g/l. of detergent solution, for 2 minutes, after aggressiveness washing and an aggressiveness iris diaphragm, perform rinse washing again, consider the cycle dried with a dehydrator as one wash, and repeat this 10 times.

[0036]** Home washing method JIS L-0217 (the 103 methods), [the solution which added 40 ** of solution temperature, and 2g/l. of detergent] a home washing machine -- the ** ratio 1:30 and a strong style -- drying during 5-minute wash-30 seconds -- the cycle dried for 30 seconds is considered as one wash after rinse washing for drying-2 minutes for rinse washing-30 seconds for -2 minutes, and this is repeated 10 times.

[0037]yellowing prepare the thing after scouring of the plain weave fabric using the worsted yarn of the pure wool of embodiment 1 wool-yarn **** 1/52, carry out compression **** of this by 65% of ***** with mangle after dipping at the treating solution of the following prescription 1, perform dry heat treatment for 2 minutes at 100 ** after dryness, and according to this invention method -- the prevention processing textile was obtained.

[0038]Prescription 1HN-130 20 g/l. (the HYDRAZINE CO. LTD. make, semi KARUBAJIDO system compound)

DENAKORUEX313 40 g/l. (made in Nagase Brothers Chemicals, Inc., polyhydric alcohol system epoxy compound)

[0039]In this example, DENAKORU EX313 was excluded from the prescription 1 for comparison with this invention, and also a processing textile for comparison (comparative example 1) was obtained by completely same method as this example. By reference, a raw textile (comparative example 2) after scouring before processing was prepared, and comparison was presented.

[0040]A fading resistance test method of a ** (1) paragraph measured and estimated the performance of this invention and a textile for comparison after practical use durability test (** and **) of said ** (2) paragraph, the result was united, and it was shown in Table 1.

[0041]

[Table 1]

		本発明	比較例 1	比較例 2
処 方	HN-130	有	有	—
	EX313	有	無	—
黄変防止性	加工上がり	○	○	×
	ドライクリーニング10回後	○	×	×
	揉み洗い洗濯(106法) 10回後	△	×	××

[0042]yellowing in which a processing textile by this invention method has practical use endurance so that more clearly than Table 1 -- it had the prevention performance.

[0043]It replaced with a thing after scouring of a plain weave fabric used in embodiment 2 above-mentioned embodiment 1, and a thing after scouring of the five-sheet satin fabric which used the cotton yarn 50/1 for warp for inside of the silk thread 21 at the woof was used, and also a processing textile of this invention was obtained by completely same method as Embodiment 1.

[0044]DENAKORU EX313 was excluded from the prescription 1 used in above-mentioned Embodiment 1 in this example 2 for comparison with this invention, and also the processing textile for comparison (comparative example 3) was obtained by the completely same method as this example. By reference, the raw textile (comparative example 4) after scouring before processing was prepared, and comparison was presented.

[0045]The fading resistance test method of the ** (1) paragraph measured and estimated the performance of this invention and the textile for comparison after the practical use durability test (** and **) of said ** (2) paragraph, the result was united, and it was shown in Table 2.

[0046]

[Table 2]

		本発明	比較例 3	比較例 4
処 方	HN 130	有	有	—
	EX313	有	無	—
黄変防止性	加工上がり	○	○	×
	ドライクリーニング10回後	○	×	×
	揉み洗い洗濯(106法) 10回後	△	×	××

[0047]yellowing in which the processing textile by this invention method has practical use endurance so that more clearly than Table 2 -- it had the prevention performance.

[0048]Supply to the solution adjusted the pH to 5 with acetic acid using the top of the Australian Merino kind materials with embodiment 3 mean fiber diameter of 20.5 micro, 2.5%

o.w.f. Add dichloro isocyanuric acid sodium in the amount of available chlorine, and it is immersed for 20 minutes at 25 **, and After a flush, 8.0% of sodium sulfite o.w.f. was added, and it processed for 15 minutes at 35 **, it washed enough, and oxidation treatment was performed. The HAKO set 57 after oxidation treatment. After processing for 20 minutes at 40 ** in addition to the treatment bath which adjusted (the Dick Hercules make and polyamide epichlorohydrin resin) to 16%o.w.f. picking, and adjusted the dilution solution to pH 8 with sodium bicarbonate, oxidation / top of resin processing shrink-proofing was obtained by drying at 80 **. Using this top of shrink-proofing, the spinning of the stockinet thread of wool yarn **** 2/60 was carried out by the usual state method, and pure wool shrink-proofing knitting of the T-cloth knitted tissue was manufactured.

[0049]. [next, a winch dyeing machine] It used, **** which adjusted 30 ml/l. of hydrogen peroxide (35%), 1g/l. of sodium pyrophosphate, and the solution of 0.5g/l. of nonionic agents to pH 8-8.5 with ammonia performed processing of 2 hours to the above-mentioned knitting at 45 **, and oxidation-bleaching processing was completed. Then, after the flush, in ****, the hydrosulfite 1g/l. was added, processing for 30 minutes was performed at 45 **, and bleaching shrink-proofing knitting was obtained.

[0050]After the treating solution of the following prescription 2 was impregnated for 10 minutes at normal temperature with the winch dyeing machine in above-mentioned bleaching shrink-proofing knitting, the tumble dryer dried and performed dry and dry heat treatment for 20 minutes at 70 ** continuously using the centrifugal dehydrator by 40% of ****, and the processing textile of this invention was obtained.

Prescription 2HN-130 40g/l.DENAKORUEX810 80 g/l. (made in Nagase Brothers Chemicals, Inc., polyhydric alcohol system epoxy compound)

[0051]In this example, DENAKORU EX810 was excluded from the prescription 2 for comparison with this invention, and also the processing textile for comparison (comparative example 5) was obtained by the completely same method as this example. By reference, the raw textile (comparative example 6) after scouring before processing was prepared, and comparison was presented.

[0052]The fading resistance test method of ** of a ** (1) paragraph and the nitric oxide gas examining method of ** measured and estimated the performance of this invention and the textile for comparison after the practical use durability test (** and **) of said ** (2) paragraph, the result was united, and it was shown in Table 3.

[0053]

[Table 3]

			本 発 明	比較例 5	比較例 6
処 方	HN-130		有	有	
	EX810		有	無	
耐 光 性 試験法	加工上がり		○	○	×
	ドライクリーニング10回後		○	×	×
黄変試験法	家庭洗濯(103法)10回後		△	×	××
	黄変試験直後		○	○	×
防 色 化	加工上がり 7日間 基 布		△	△	××
	放置後 添付布		○	○	×
窒 素 止 ガ ス 試験法	ドライクリーニング 7日間 基 布		○	×	×
	放置後 添付布		○	×	×
性	家庭洗濯 (103法) 10回後		△	×	×
	黄変試験直後		△	×	×
	7日間 基 布		△	××	××
	放置後 添付布		○	×	×

[0054]comparing a raw textile (comparative example 6) with turning yellow greatly by the practical use washing treatment of dry cleaning and the 103 methods so that more clearly than the column of the fading resistance test method of Table 3 -- yellowing of this invention -- yellowing where the textile which gave prevention processing also had little yellowing and which was excellent -- it turns out that it has the prevention effect. moreover -- comparing with raw bleaching shrink-proofing knitting (comparative example 6) having turned yellow so that more clearly than the column of the nitric oxide gas examining method of the table -- yellowing of this invention -- yellowing which was excellent in the prevention processing textile -- it turns out that it has the prevention effect. furthermore -- in the result after the neglect during seven days -- foundation cloth and an attachment cloth -- yellowing of this invention -- yellowing is seldom accepted but, moreover, also sets a prevention processing textile on the attachment cloth after neglect for seven days -- yellowing of this invention -- it turns out that the prevention processing textile also has the effect of preventing yellowing by **** of a phenol system derivative.

[0055]In the embodiment 4 above-mentioned embodiment 3, before processing the treating solution of the prescription 2 to bleaching shrink-proofing knitting with a winch dyeing machine, the following prescription 3 dyes for 60 minutes at 98 **, and also. This invention and the processing textile for comparison (what does not contain EX810 is made into the comparative example 7, and a raw textile is made into the comparative example 8.) were obtained by the completely same method as Embodiment 3.

Prescription 3 (gray)

Lanyl Grey B 1.0%o.w.f. (the SUMITOMO CHEMICAL COMPANY LIMITED make, **** dye)
 Albegal A 1.0%o.w.f. (the product made by Ciba-Geigy, a leveling agent)
 [0056]The ***** method of ** of a ** (1) paragraph measured and estimated the performance of this invention and the processing textile for comparison after the practical use durability test (** and **) of said ** (2) paragraph, the result was united, and it was shown in Table 4.

[0057]

[Table 4]

		本 発 明		比較例 7	比較例 8
処 方	INN-130	有	有		
	EX810	有	無		
変 更 助 止 性	加工工程がわ	DL*	0.2	0.3	0.5
		Da*	1.0	1.0	3.2
		Db*	0.7	0.8	1.8
		DE*	1.2	1.3	3.7
	ドライクリーニング後	DL*	0.1	-0.4	-0.7
		Da*	1.1	2.7	3.5
		Db*	0.9	1.7	2.4
		DE*	1.4	3.2	4.3
	家庭洗濯(103法)後	DL*	0.0	0.6	-0.8
		Da*	1.2	3.0	3.7
		Db*	1.1	1.8	2.7
		DE*	1.6	3.5	4.8

[0058]From Table 4 so that clearly, [the raw textile of the comparative example 8] comparing with hue having been tinged with yellow and having turned yellow by practical use wash of dry cleaning and the 103 methods, -- yellowing of this invention -- a prevention processing textile has a small hue difference in which after dry cleaning and the 103 method practical use washing treatment includes yellowing as well as processing going up, and it turns out that it has the outstanding effect.

[0059]In the embodiment 5 above-mentioned embodiment 4, replaced with the prescription 3, and the following prescription 4 was used, and also this invention and the processing textile for comparison (what does not contain EX810 is made into the comparative example 9, and a raw textile is made into the comparative example 10.) were obtained by the completely same method as Embodiment 4.

Prescription 4 (beige)

Lanyl Brown GR 0.2%o.w.f. (the SUMITOMO CHEMICAL COMPANY LIMITED make, **** dye)

Lanyl Orange R 0.2%o.w.f.

(The SUMITOMO CHEMICAL COMPANY LIMITED make, **** dye)

[0060]The ***** method of ** of a ** (1) paragraph measured and estimated the performance of this invention and the processing textile for comparison after the practical use durability test

United States Patent [19]

Bouwknegt et al.

[11] Patent Number: 5,069,681

[45] Date of Patent: Dec. 3, 1991

[54] PROCESS FOR THE PHOTOCHEMICAL STABILIZATION OF DYED POLYAMIDE FIBRES WITH FOAMED AQUEOUS COMPOSITION OF COPPER ORGANIC COMPLEXES

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[73] Assignee: Ciba-Geigy Corporation, Ardsley, N.Y.

[21] Appl. No.: 633,832

[22] Filed: Dec. 26, 1990

[30] Foreign Application Priority Data

Jan. 3, 1990 [CH] Switzerland 10/90

[51] Int. Cl.³ D06P 5/02

[52] U.S. Cl. 8/442; 8/477; 8/575; 8/602; 8/607; 8/608; 8/624; 8/924

[58] Field of Search 8/442, 477

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Primary Examiner—A. Lionel Clingman
Attorney, Agent, or Firm—George R. Dohmann;
Edward McC. Roberts

ABSTRACT

There is disclosed a process for the photochemical stabilization of dyed polyamide fibre materials, which comprises treating the dyed material with an aqueous foamed composition which contains at least a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes.

By means of the process of this invention it is possible to prevent wastewater from being contaminated with copper-containing impurities.

24 Claims, No Drawings

PROCESS FOR THE PHOTOCHEMICAL STABILIZATION OF DYED POLYAMIDE FIBRES WITH FOAMED AQUEOUS COMPOSITION OF COPPER ORGANIC COMPLEXES

The present invention relates to a process for the photochemical stabilisation of dyed polyamide fibre materials, preferably of marked three-dimensional character (pile materials) and, in particular, carpets with the aid of foam, to an aqueous composition for carrying out said process, and to the textile material treated by said process.

The use of copper complexes of bisazomethines for enhancing the lightfastness of dyeings on polyamide fabric is taught in U.S. Pat. No. 4,655,783, which copper complexes are applied in the dyebath. This process results unavoidably in waste liquors which are contaminated with copper.

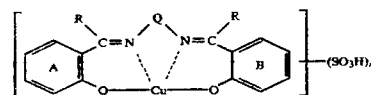
Surprisingly, it has proved possible to prevent these contaminated waste liquors by applying these copper complexes to the dyed textile material in an aftertreatment by means of an foamed aqueous composition.

Specifically, the invention relates to a process for the photochemical stabilisation of dyed polyamide fibre materials, which comprises treating the dyed material with a foamed aqueous composition which contains at least

(a) a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes.

Bisazomethines of aromatic aldehydes or ketones are here understood to mean Schiff base of aliphatic or aromatic diamines, the aldehydes and ketones having an OH group in the o-position to the formyl or acetyl radical. They are bonded to the metal atom via these two OH groups and the two nitrogen atoms in the bisazomethine moiety. Accordingly, these are quadridentate ligands, which can contain one or more sulfo groups which are located in the aldehyde or ketone moiety and/or in the bisazomethine bridge.

The component (a) used is preferably a copper complex of the formula



in which R is hydrogen or a substituted or unsubstituted alkyl or aryl radical, Q is a substituted or unsubstituted alkylene, cycloalkylene or arylene radical and n is 0, 1, 2 or 3.

The benzene ring A and B can also be substituted, and in particular independently of one another.

A substituted or unsubstituted alkyl radical R can preferably be a C₁-C₈alkyl radical, especially a C₁-C₄alkyl radical, which can be branched or unbranched and can be unsubstituted or substituted, namely by halogen such as fluorine, chlorine or bromine, C₁-C₈alkoxy such as methoxy or ethoxy, by a phenyl or carboxyl radical, by C₁-C₈alkoxycarbonyl, for example the acetyl radical, or by hydroxyl or a mono- or di-alkylated amino group. Furthermore, a cyclohexyl radical is also

5,069,681

2

possible, which can likewise be substituted, for example by C₁-C₈alkyl or C₁-C₈alkoxy.

A substituted or unsubstituted aryl radical R can especially be a phenyl or naphthyl radical which can be substituted by C₁-C₈alkyl such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl, C₁-C₈alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy and tert-butoxy, halogen such as fluorine, chlorine or bromine, C₂-C₈alkanoylamino such as acetylamino, propionylamino or butyrylamino, nitro, cyano, sulfo or a mono- or di-alkylated amino group.

An alkylene radical Q is especially a substituted or unsubstituted C₂-C₈alkylene radical, in particular a —CH₂—CH₂ bridge. However, this can also be a C₂-C₈alkylene chain interrupted by oxygen or especially by nitrogen, and in particular a —(CH₂)₃—NH—(CH₂)₃— bridge.

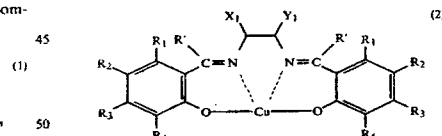
An arylene radical Q is especially a phenylene radical, in particular an o-phenylene radical. This can be substituted by C₁-C₈alkyl or C₁-C₈alkoxy.

A cycloalkylene radical Q is a cycloaliphatic radical of 5-7 carbon atoms, such as cyclopentylene, cyclohexylene or cycloheptylene.

Possible substituents for the benzene rings A and B are: halogen such as fluorine, chlorine or bromine, the cyano or nitro group, alkyl, alkoxy, hydroxyl, hydroxyalkyl, alkoxyalkoxy, alkoxyalkoxyalkoxy, carboxymethoxy, alkylamino, dialkylamino, —SO₂NH₂, —SO₂NHR₀ or —SO₂N(R₀), R₀ being alkyl or alkoxyalkyl, and alkyl and alkoxy each being understood as radicals having 1-4 carbon atoms, or a benzene radical formed by radicals in the mutual ortho-positions, together with the carbon atoms to which they are linked.

The sulfo group(s) in the benzene rings A and/or B and/or in the bridge member Q, if the latter is an arylene radical, is (are) preferably in the form of an alkali metal salt, especially as the sodium or as an amine salt.

Amongst the copper complexes of formula (1) particular importance is attached to the bisazomethine complexes of the formula



in which R' is hydrogen, R₁, R₂, R₃ and R₄ are each hydrogen, halogen, hydroxyl, hydroxyalkyl, alkyl, alkoxy, alkoxyalkoxy, alkoxyalkoxyalkoxy, carboxymethoxy, alkylamino, dialkylamino, —SO₂NH₂, —SO₂NHR₀ or —SO₂N(R₀), R₀ being alkyl or alkoxyalkyl, and alkyl or alkoxy each being understood as groups having 1-4 carbon atoms, or R₁ and R₂ or R₃ or R₄, together with the carbon atoms to which they are linked, form a benzene radical, and X₁ and Y₁ are hydrogen, C₁-C₈alkyl or an aromatic radical or X₁ and Y₁ form together with the carbon atom to which they are linked a cycloaliphatic radical of 5-7 carbon atoms.

X₁ and X₂ in the meaning of C₁-C₈alkyl are for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl. Aromatic radicals for X₁ and

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Y₁ are in particular substituted or not substituted naphthyl and most particular phenyl radicals.

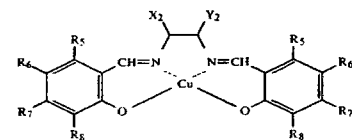
The cycloaliphatic radicals are cyclopentylene, cyclohexylene or cycloheptylene radicals.

The copper complex compounds of formula (2) are normally water-insoluble, provided they contain no carboxymethoxy radicals ($-\text{O}-\text{CH}_2-\text{COOH}$) or salts thereof.

Preferably R₁ to R₄ are each independently of the other hydrogen, chloro, bromo, methyl, ethyl, butyl, methoxy, ethoxy, methoxyethoxy, ethoxyethoxyethoxy or diethylamino, or R₁ and R₂ together form a fused benzene ring.

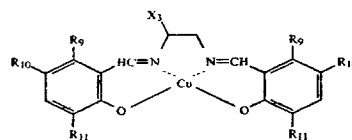
One of the substituents X₁ and Y₁ is preferably hydrogen and the other is hydrogen, methyl, ethyl or phenyl, or X₁ and Y₁ together form a cyclohexylene radical.

Preferably water-insoluble copper complex compounds of the formula



are used wherein R₅ to R₈ are each and independently from each other hydrogen, hydroxyl, chlorine, bromine, methyl, tert-butyl, methoxy, methoxyethoxy, ethoxyethoxyethoxy or diethylamino, X₂ hydrogen, methyl, ethyl or phenyl and Y₂ hydrogen or R₅ and R₆ together form a fused benzene ring or X₂ and Y₂ together form a cyclohexylene radical.

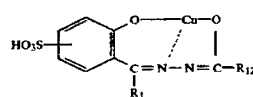
Of particular interest are compounds of the formula



wherein R₉, R₁₀ and R₁₁ are each independently of one another hydrogen, chloro, bromo, methyl or methoxy, or wherein R₉ and R₁₀ together form a fused benzene ring, and X₃ is hydrogen, methyl, ethyl or phenyl.

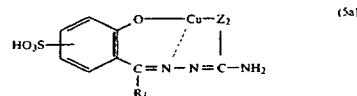
Particularly preferred, however, are compounds of formula (4), wherein R₉, R₁₀, R₁₁ and X₃ are hydrogen.

Copper complexes of acylhydrazones of aromatic aldehydes and ketones as component (a) are especially the complex compounds of formula



in which R₁ and R₁₂ independently of one another are hydrogen or a substituted or unsubstituted alkyl or aryl radical, and copper complexes of semicarbazones or

thiosemicarbazones as the component (a) are especially the complexes of the formula



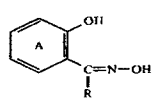
in which R₁ is as defined in formula (5) and Z₂ is oxygen or sulfur.

The alkyl radical R₁ and/or R₁₂ in the formulae (5) and (5a) can be branched or unbranched and has a chain length of preferably 1 to 8 and especially 1 to 4 carbon atoms. Possible substituents are halogen such as fluorine, chlorine or bromine, C₁-C₄alkoxy such as methoxy or ethoxy, and also phenyl or carboxyl, C₁-C₄alkoxycarbonyl, for example acetyl, or hydroxyl and mono- or dialkylamino.

A substituted or unsubstituted aryl radical R₁ and/or R₁₂ in the formulae (5) and (5a) can especially be a phenyl or naphthyl radical which can be substituted by C₁-C₄alkyl such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl, C₁-C₄alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy, halogen such as fluorine, chlorine or bromine, C₂-C₃alkanoylamino such as acetylamino, propionylamino or butyrylamino, nitro, cyano, sulfo or a mono- or di-alkylated amino group.

Those complexes of the formula (5) are preferably used in which R₁ is hydrogen and R₁₂ is hydrogen, methyl or especially a phenyl radical, and particularly the complexes in which the sulfo group in turn is in the p-position to the oxygen.

Copper complexes of oximes as component (a) are mainly copper compounds of phenols of the formula



wherein R is hydrogen, hydroxy, alkyl or cycloalkyl, and in which the ring A can be substituted or further substituted, for example copper compounds of salicylaldehyde and salicylhydroxamic acid.

Suitable alkyl radicals are those having 1 to 4 carbon atoms, suitable cycloalkyl radicals cyclohexyl and methylcyclohexyl radicals, suitable substituents in the ring A are methyl, methoxy or chlorine. However, this ring is preferably unsubstituted.

The complexes of the formulae (1) to (5) are preferably used in the neutral form, viz. as an alkali metal salt, in particular the sodium salt, or an amine salt.

The compounds which can be used as component (a) are known and can be prepared by processes known per se. They are known for example from EP-A 51 188, 113 856 and 162 811 can be prepared by known processes.

The compounds which can be used as component (a) are conveniently applied from an aqueous bath, preferably in an amount such that 5 to 200 µg, preferably 10 to 100 µg, of copper are applied per 1 g of polyamide fibre material.

5
If the compounds of formula (1) are not water soluble they are conveniently used as fine dispersions which are obtained by milling in the presence of customary dispersants.

The foamed aqueous composition comprises, in addition to component (a),

(b) an anionic surfactant or a nonionic surfactant or a mixture of such surfactants, and, as optional components,

(c) a salt of a hydrolysed polymaleic anhydride, and (d) a polar organic solvent.

Component (b) of the composition of this invention is the actual foaming agent. Suitable for use as component (b) are anionic or nonionic surfactants or mixtures of anionic and nonionic surfactants.

The anionic surfactants of component (b) are preferably polyadducts of alkylene oxide, for example polyadducts of alkylene oxides, preferably of ethylene oxide and/or propylene oxide or also styrene oxide, with organic hydroxyl, carboxyl, amino and/or amido compounds or mixtures thereof containing aliphatic hydrocarbon radicals having a total of at least two carbon atoms, which adducts contain acid ether groups or, preferably, acid ester groups of inorganic or organic acids. These acid ethers or esters may be in the form of free acids or of salts, for example alkali metal salts, alkaline earth metal salts, ammonium salts or amine salts.

These anionic surfactants are prepared by known methods by addition of at least 1 mol, preferably of more than 1 mol, typically 2 to 60 mol, of ethylene oxide or propylene oxide or, alternately in any order, ethylene oxide and propylene oxide, to the above organic compounds, and subsequently esterifying the adducts, and, if desired, converting the esters into their salts. Suitable starting materials are, for example, higher fatty alcohols, i.e. alkanols or alkenols, each containing 8 to 22 carbon atoms, dihydric to hexahydric alcohols containing 2 to 9 carbon atoms, alicyclic alcohols, phenylphenols, benzylphenols, alkylphenols containing one or more alkyl substituents which together contain at least 4 carbon atoms, fatty acids containing 8 to 22 carbon atoms, amines which contain aliphatic and/or cycloaliphatic hydrocarbon radicals of at least 8 carbon atoms, preferably fatty amines which contain such radicals, hydroxyalkylamines, hydroxyalkylamides and aminoalkyl esters of fatty acids or dicarboxylic acids and higher alkylated aryloxy-carboxylic acids.

Illustrative examples of suitable anionic surfactants are:

sulfated aliphatic alcohols containing 8 to 18 carbon atoms in the alkyl chain, for example sulfated lauryl alcohol;

sulfated unsaturated fatty acids or lower alkyl esters of fatty acids which contain 8 to 20 carbon atoms, for example ricinoleic acid and oils containing such fatty acids, for example castor oil;

alkylsulfonates containing 8 to 20 carbon atoms in the alkyl chain, for example dodecylsulfonate;

alkylarylsulfonates having a straight or branched alkyl chain containing at least 6 carbon atoms, for example dodecylbenzenesulfonates or 3,7-disubstituted naphthalenesulfonates;

the alkali metal salts, ammonium salts or amine salts of fatty acids of 10 to 20 carbon atoms referred to as soaps, for example colophonium salts;

esters of polyalcohols, preferably mono- or diglycerides of fatty acids containing 12 to 18 carbon atoms, for

example monoglycerides of lauric, stearic or oleic acid, and

the polyadducts of 1 to 60 mol of ethylene oxide and/or propylene oxide with fatty amines, fatty acids or fatty alcohols, each containing 8 to 22 carbon atoms, with alkylphenols containing 4 to 16 carbon atoms in the alkyl chain, or with trihydric to hexahydric alcohols containing 3 to 6 carbon atoms, which polyadducts are converted into an acid ester with an organic dicarboxylic acid such as maleic acid, malonic acid or sulfosuccinic acid, but preferably with an inorganic polybasic acid such as o-phosphoric acid or, more particularly, sulfuric acid.

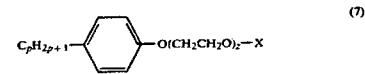
Anionic surfactants very suitable for use as component (b) are:

(I) acid esters, or their salts, of a polyadduct of 2 to 15 mol of ethylene oxide with 1 mol of a fatty alcohol containing 8 to 22 carbon atoms or with 1 mol of an alkylphenol containing 4 to 12 carbon atoms in the alkyl moiety,

(II) alkylphenylsulfonates containing 8 to 18 carbon atoms in the alkyl moiety,

(III) sulfonated 1-benzyl-2-alkylbenzimidazoles containing 8 to 22 carbon atoms in the alkyl moiety, which components (I), (II) and (III) may be used singly or in admixture.

Component (I) of above preferred anionic surfactants can be represented, for example, by the formula



or by the formula



wherein R is alkyl or alkenyl, each of 8 to 22 carbon atoms, X is the acid radical of an inorganic, oxygen-containing acid or the radical of an inorganic acid, p is 4 to 12 and z is 2 to 15.

The alkyl radicals in the benzene ring of formula (7) may be butyl, hexyl, n-octyl, n-nonyl, p-tert-octyl, p-tert-nonyl, decyl or dodecyl. Alkyl radicals of 8 to 12 carbon atoms are preferred, especially the octyl and nonyl radicals.

The acid radical X is derived from, for example, low molecular dicarboxylic acids such as maleic acid, malonic acid, succinic acid or sulfosuccinic acid, and is linked via an ester bridge to the ethyleneoxy moiety of the molecule. In particular, however, X is derived from inorganic polybasic acids such as orthophosphoric acid and, preferably, sulfuric acid. The acid radical X is preferably in salt form, i.e. for example as alkali metal salt, alkaline earth metal salt, ammonium salt or amine salt. Exemplary of such salts are lithium, sodium, potassium, ammonium, trimethylamine, ethanolumine, diethanolamine or triethanolamine salts.

The fatty alcohols for preparing component (I) of formula (8) are typically those containing 8 to 22, preferably 8 to 18, carbon atoms, and are, for example, octyl, decyl, lauryl, tridecyl, myristyl, cetyl, stearyl, oleyl, arachidyl or behenyl alcohol.

Ester formation is normally effected with the same acids as have been cited for compounds of formula (7).

A preferred compound of formula (8) is the sodium salt of lauryl triglycol ether sulfonic acid.

The following compounds are cited in particular for component (I) of formulae (4) and (5):

1. the ammonium salt of the sulfated polyadduct of 2 mol of ethylene oxide with 1 mol of *p*-tert-nonylphenol;
2. the sodium salt of the monomaleate of the polyadduct of 2 mol of ethylene oxide with 1 mol of *p*-nonylphenol;
3. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of *p*-butylphenol;
4. the ammonium salt of the phosphated polyadduct of 2 mol of ethylene oxide with 1 mol of *p*-nonylphenol;
5. the sodium salt of the disulfosuccinate of the polyadduct of 4 mol of ethylene oxide with 1 mol of *n*-octylphenol;
6. the ammonium salt of the sulfated polyadduct of 9 mol of ethylene oxide with 1 mol of *p*-nonylphenol;
7. the ammonium salt of the sulfated polyadduct of 6 mol of ethylene oxide with 1 mol of *p*-nonylphenol;
8. the sodium salt of the monosulfosuccinate of the polyadduct of 2 mol of ethylene oxide with 1 mol of *p*-nonylphenol;
9. the ammonium salt of the sulfated polyadduct of 6 mol of ethylene oxide with 1 mol of dodecylphenol;
10. the ammonium salt of the sulfated polyadduct of 2 mol of ethylene oxide with 1 mol of octylphenol;
11. the ammonium salt of the sulfated polyadduct of 2 mol of ethylene oxide with 1 mol of Alfol (1014);
12. the ammonium salt of the sulfated polyadduct of 2 mol of ethylene oxide with 1 mol of stearyl alcohol;
13. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of 2-ethylhexanol;
14. the ammonium salt of the sulfated polyadduct of 15 mol of ethylene oxide with 1 mol of stearyl alcohol;
15. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of tridecyl alcohol;
16. the ammonium salt of the sulfated polyadduct of 4 mol of ethylene oxide with 1 mol of hydroabietyl alcohol;
17. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of Alfol (2022);
18. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of lauryl alcohol;
19. the bis(β -hydroxyethyl)amine salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of lauryl alcohol;
20. the sodium salt of the sulfated polyadduct of 2 mol of ethylene oxide with 1 mol of lauryl alcohol;
21. the sodium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of lauryl alcohol;
22. the phosphated polyadduct of 5 mol of ethylene oxide with 1 mol of 2-ethyl-n-hexanol;
23. the ammonium salt of the sulfated polyadduct of 3 mol of ethylene oxide with 1 mol of a mixture of alcohols containing 20 to 22 carbon atoms;
24. the diphosphate of the polyadduct of the 8 mol of ethylene oxide with 1 mol of dodecylamine;
25. the ammonium salt of the phosphated polyadduct of 8 mol of ethylene oxide with 1 mol of tallow fatty amine.

The alkylphenyl sulfonates of component (II) are normally alkali metal salts of corresponding monosulfonic acids containing 8 to 18 carbon atoms in the alkyl moiety, which may be straight-chain or branched and saturated or unsaturated. Suitable alkyl radicals are,

typically, *n*-octyl, *tert*-octyl, *n*-nonyl, *tert*-nonyl, *n*-decyl, *n*-dodecyl, tridecyl, myristyl, cetyl, stearyl or oleyl. Alkyl radicals of 8 to 12 carbon atoms are preferred and dodecylbenzenesulfonate (sodium salt) is particularly preferred.

Components (I) and (II) may be used alone or in admixture with each other.

The nonionic surfactants of component (b) are conveniently nonionic polyadducts of 1 to 100 mol of alkylene oxide, for example ethylene oxide and/or propylene oxide, with 1 mol of an aliphatic monoalcohol containing at least 4 carbon atoms, of a trihydric to hexahydric aliphatic alcohol, of an unsubstituted or of an alkyl- or phenyl-substituted phenol or of a fatty acid containing 8 to 22 carbon atoms.

The aliphatic monoalcohols for obtaining the nonionic surfactants are, for example, water-soluble monoalcohols containing at least 4, preferably 8 to 22, carbon atoms. These alcohols may be saturated or unsaturated and straight-chain or branched, and they may be used singly or in admixture. A natural alcohol such as myristyl alcohol, cetyl alcohol, stearyl alcohol or oleyl alcohol, or a synthetic alcohol, preferably 2-ethylhexanol and also trimethylhexanol, trimethylnonyl alcohol, hexadecyl alcohol or a fatty alcohol, may be reacted with the alkylene oxide.

Further aliphatic alcohols which may be reacted with the alkylene oxide are trihydric to hexahydric alkanols. These alcohols contain 3 to 6 carbon atoms and are preferably glycerol, trimethylolpropane, erythritol, mannitol, pentaerythritol and sorbitol. The trihydric to hexahydric alcohols are preferably reacted with propylene oxide or ethylene oxide or with mixtures thereof.

Illustrative examples of unsubstituted or substituted phenols are phenol, *o*-phenylphenol or alkylphenols which contain 1 to 16, preferably 4 to 12, carbon atoms in the alkyl moiety. Exemplary of these alkylphenols are *p*-cresol, butylphenol, tributylphenol, octylphenol and, preferably, nonylphenol.

The fatty acids preferably contain 8 to 12 carbon atoms and may be saturated or unsaturated. Typical examples of such fatty acids are capric, lauric, myristic, palmitic or stearic acid, and decenoic, dodecenoic, tetradecenoic, hexadecenoic, oleic, linoleic, linolenic or, preferably, ricinolic acid.

Illustrative examples of nonionic surfactants suitable for use as component (b) are:

polyadducts of preferably 5 to 80 mol of alkylene oxides, preferably ethylene oxide, in which individual ethylene oxide units may be replaced by substituted epoxides such as styrene oxide and/or propylene oxide, with higher unsaturated or unsaturated fatty alcohols, fatty acids, fatty amines or fatty amides containing 8 to 22 carbon atoms or with phenylphenol or alkylphenols, whose alkyl moieties contain at least 4 carbon atoms;

alkylene oxide condensates, preferably ethylene oxide and/or propylene oxide condensates

reaction products of a fatty acid containing 8 to 22 carbon atoms and a primary or secondary amine having at least one hydroxy-lower alkyl or lower alkoxy-lower alkyl group, or polyadducts of alkylene oxide with these hydroxyalkylated reaction products, the reaction taking place such that the molecular ratio of hydroxyalkylamine to fatty acid may be 1:1 and greater than 1, for example 1.1:1 to 2:1, and polyadducts of propylene oxide with a trihydric to hexahydric aliphatic alcohol of 3 to 5 carbon atoms,

for example glycerol or pentaerythritol, said polypropylene oxide polyadducts having an average molecular weight of 250 to 1800, preferably 400 to 900.

Nonionic surfactants very suitable for use as component (b) are:

(IV) polyadducts of 2 to 15 mol of ethylene oxide with 1 mol of a fatty alcohol or fatty acid, each containing 8 to 22 carbon atoms, or with 1 mol of alkylphenol containing a total of 4 to 12 carbon atoms in the alkyl moiety,

(V) fatty alcohols or mono-, di- or triethoxylated fatty alcohols containing 8 to 22 carbon atoms in the fatty alcohol radical, or

(VI) fatty acid diethanolamides containing 8 to 22 carbon atoms in the fatty acid radical.

Component (IV) is suitably a polyadduct of octylphenol or, preferably, of nonylphenol, with ethylene oxide, which polyadduct contains 2 to 12 ethylene oxide units.

The following compounds may be specifically mentioned: *p*-octylphenol/2 mol of ethylene oxide, *p*-nonylphenol/9 mol of ethylene oxide, *p*-nonylphenol/10 mol of ethylene oxide, *p*-nonylphenol/11 mol of ethylene oxide.

Further polyadducts of an alkylphenol with ethylene oxide can be derived from, for example, butylphenol or tributylphenol.

Component (IV) may conveniently also be a polyadduct of 2 to 15 mol, preferably 7 to 15 mol, of ethylene oxide with 1 mol of an aliphatic monoalcohol containing 8 to 22 carbon atoms.

The aliphatic monoalcohols may be saturated or unsaturated and used singly or in admixture. Natural alcohols such as lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, or synthetic alcohols, preferably 2-ethylhexanol, and also trimethylhexanol, trimethylnonyl alcohol, hexadecyl alcohol or C_{12} - C_{22} fatty alcohols, may be reacted with ethylene oxide.

Polyadducts of 2 to 15 mol of ethylene oxide with 1 mol of fatty acid may also be used as component (IV). The fatty acids preferably contain 10 to 20 carbon atoms and may be saturated or unsaturated. Typical examples of such fatty acids are capric, lauric, myristic, palmitic or stearic acid, and decenoic, dodecenoic, tetradecenoic, hexadecenoic, oleic, linoleic, or ricinolic acid.

Component (V) is a fatty alcohol or an ethoxylated fatty alcohol as defined herein having a HLB value of preferably 0.1 to 10, most preferably of 0.5 to 10. Components (V) having HLB values in the range from 0.1 to 7.0 have been found to be particularly useful. The HLB value is an indication of the hydrophilic/lipophilic balance in a molecule. The HLB values can be determined experimentally or computed in accordance with W. C. Griffin, ISCC 5, 249 (1954) or J. T. Davis, Tenside Detergents 11 (3), 133 (1974).

The fatty alcohols suitable for use as component (V) may be saturated or unsaturated. They preferably contain 12 to 18 carbon atoms. Illustrative examples of such alcohols suitable for use as component (V) are: lauryl, myristyl, cetyl, stearyl, oleyl, arachidyl, behenyl alcohol or C_{12} - C_{22} fatty alcohols.

These fatty alcohols may be conveniently be mono-, di- or triethoxylated.

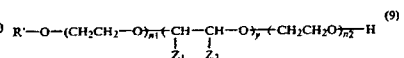
Preferred components (V) are cetyl alcohol or diethylene glycol cetyl ether (=polyoxyethylene-(2)-cetyl ether) of formula $C_{16}H_{33}-O-(CH_2CH_2O)_n-H$.

The fatty acid alkanolamine reaction products of component (VI) are typically products which are prepared from fatty acids of 8 to 22, preferably 8 to 18, carbon atoms, and alkanolamines of 2 to 6 carbons such as ethanolamine, diethanolamine, isopropanolamine or diisopropanolamine. Diethanolamine is preferred. Fatty acid diethanolamines containing 8 to 18 carbon atoms are especially preferred.

Exemplary of suitable fatty acids are caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, oleic, linoleic, linolenic, arachidonic or coconut fatty acid.

Preferred examples of such reaction products are coconut fatty acid diethanolamide and lauric acid or stearic acid diethanolamide.

Further very suitable nonionic surfactants are alkylene oxide polyadducts of formula



wherein R' is hydrogen, alkyl or alkenyl of at most 18 carbon atoms, preferably of 8 to 16 carbon atoms, *o*-phenylphenyl or alkylphenyl containing 4 to 12 carbon atoms in the alkyl moiety, one of Z_1 and Z_2 is hydrogen and the other is methyl, y is 1 to 15, and the sum of $n_1 + n_2$ is 3 to 15.

Particularly useful nonionic surfactants are fatty alcohol polyglycol mixed ethers, preferably adducts of 3 to 10 mol of ethylene oxide and 3 to 10 mol of propylene oxide with aliphatic monoalcohols of 8 to 16 carbon atoms.

The following polyadducts are exemplary of alkylene oxide polyadducts of formula (9):

- a1. polyadduct of 12 mol of ethylene oxide and 12 mol of propylene oxide with 1 mol of a C_4 - C_{18} fatty alcohol,
- a2. polyadduct of 5 mol of ethylene oxide and 5 mol of propylene oxide with 1 mol of a C_{12} - C_{14} fatty alcohol,
- a3. polyadduct of 9 mol of ethylene oxide and 7 mol of propylene oxide with 1 mol of a C_{16} - C_{18} fatty alcohol,
- a4. polyadduct of 9.5 mol of ethylene oxide and 9.5 mol of propylene oxide with 1 mol of nonylphenol.

For component (b) it is preferred to use a combination of components (I), (II), (III), (IV), (V) and (VI). The composition of this invention preferably contains, as component (a), a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes and, as component (b), a combination of components (I), (II), (III), (IV), (V) and (VI).

The composition of this invention most preferably contains, as component (a), a copper complex of formula (2), and, as component (b), a combination of components (I), (II), (III), (IV), (V) and (VI).

Particularly preferred mixtures of component (b) are, typically, those of

(1) nonylphenol/ethylene oxide polyadducts containing 10 to 12 ethylene oxide units, sodium salts of sulfated fatty alcohol ethylene oxide polyadducts containing 8 to 12 carbon atoms in the alcohol moiety and 2 to 4 ethylene oxide units and coconut fatty acid diethanolamide,

(2) reaction products of 7 to 15 mol of ethylene oxide with 1 mol of stearyl alcohol, coconut fatty acid

diethanolamide and cetyl alcohol or diethoxylated cetyl alcohol, or
(3) dodecylbenzenesulfonate, sodium lauryl triglycol ether sulfate, coconut fatty acid diethanolamide and the disodium salt of 1-benzyl-2-stearylbenzimidazolesulfonic acid.

Particularly preferred are mixtures of a sulfated polyadduct of a fatty alcohol and ethylene oxide containing 8 to 18 carbon atoms in the alcohol moiety and 2 to 4 ethylene oxide units, or the alkali metal salt thereof, and a fatty acid diethanolamide containing 8 to 18 carbon atoms in the fatty acid moiety.

A mixture of sodium lauryl triglycol ether sulfate and fatty acid diethanolamide is particularly preferred.

The compounds of component (b) are very good foaming agents, i.e. they are able on the one hand to form the foam to a sufficient degree when used in small amounts and, on the other, also to stabilise the foam.

The optional component (c) of the composition of this invention is hydrolysed polymaleic anhydride, which suitably has a molecular weight of 300 to 5000 and is at least partially in the form of a water-soluble salt of such a polymaleic anhydride. Polymers of this kind are suitable chelating agents for binding contaminants present in the fibre material, for example calcium and/or magnesium salts.

Polymaleic anhydride is a homopolymer of maleic anhydride and can be very readily hydrolysed, for example by heating with water, to form a polymeric product. The product does not constitute a pure polymaleic acid. The exact constitution of the product is not known. Hence within the scope of this invention, this polymeric product formed by hydrolysis of polymaleic anhydride will be referred to as hydrolysed polymaleic anhydride. This hydrolysed polymaleic anhydride can be prepared from a polymer by addition polymerisation of a starting monomer consisting essentially of maleic anhydride under polymerisation conditions in the melt or by solution polymerisation. It is preferred to polymerise maleic anhydride in an inert organic solvent such as toluene or xylene, in the presence of a polymerisation catalyst, preferably of a radical initiator such as benzoyl peroxide, di-tertiary butyl peroxide or monobutyl peroxide, in the temperature range up to 150° C., for example in the range from 120° to 145° C. The main chain of the primary polymer is formed essentially by non-hydrolysable bonds. After being freed from unreacted monomer and other nonpolymeric constituents, the primary non-hydrolysed polymer product is then hydrolysed with water or a water-soluble alkali and so used. In some cases, it can also be added in non-hydrolysed form to the aqueous treatment baths.

During the polymerisation or after the subsequent hydrolysis, a decarboxylation of the polymer may occur, so that the acid number found of the hydrolysed polymaleic anhydride is lower than the theoretical value of 1143 mg KOH/g. Such a decarboxylation, however, does not take place to such an extent that the acid number falls below 350 mg KOH/g. The acid number can be determined by potentiometric titration in aqueous solution against 0.1N potassium hydroxide solution, plotting $\Delta pH/\Delta V$ graphically and taking the highest peak as the end point. ΔpH represents the change in pH, ΔV the change in volume, and V the titrated volume.

It is important that the molecular weight of the hydrolysed polymaleic anhydride should lie in the indicated low range. It is preferred to use polymaleic anhydride having a molecular weight which does not exceed 2000 and which is preferably in the range from 350 to 1000.

The molecular weight of the polymaleic anhydride is normally calculated from the osmometric data of the polymaleic anhydride before the hydrolysis.

Further particulars on the nature of the hydrolysed polymaleic anhydride and the preparation thereof are disclosed in British patent specifications 1 369 429, 1 411 063 and 1 491 978, and in Swiss patent specification 624 256.

By addition of bases to the hydrolysed polymaleic anhydride, the carboxyl groups are in the form of water-soluble salt groups when using medium-strong to strong bases. When using weak bases, only some of the carboxyl groups are in the form of water-soluble salts. Exemplary of salt groups are alkali metal salts, alkylammonium salts, alkanolammonium salts or ammonium salts. Alkali metal salts are in particular the sodium or potassium salt, and alkylammonium or alkanolammonium salts are the trimethylammonium, monoethanolammonium, diethanolammonium or triethanolammonium salt. The sodium or ammonium salt is preferred.

As component (c), the salt of hydrolysed polymaleic anhydride of the indicated kind is normally in the form of an aqueous solution of ca. 40-60% by weight.

Suitable polar organic solvents for optional component (d) of the process of this invention are solvents which are preferably soluble in water in any ratio. Component (d) serves to improve the solubility of the individual components. Illustrative examples of water-soluble organic solvents are aliphatic C₁-C₁₀ alcohols such as methanol, ethanol or the propanols; alkylene glycols such as ethylene glycol or propylene glycol; monoalkyl ethers of glycols such as ethylene glycol monomethyl, monoethyl or monobutyl ether, and diethylene glycol monomethyl or monoethyl ether; ketones such as acetone, methyl ethyl ketone, cyclohexanone, diacetone alcohol; ethers and acetals such as diisopropyl ether, diphenyl oxide, dioxane, tetrahydrofuran, and also tetrahydrofurfuryl alcohol, pyridine, acetonitrile, γ -butyrolactone, N,N-dimethylformamide, N,N-dimethylacetamide, tetramethylurea and tetramethylenesulfone. Mixtures of the cited solvents may also be used. Preferred solvents are the cited alcohols, monoalkyl ethers of the glycols and ketones of the indicated kind, especially the ethylene glycols such as ethylene glycol and, preferably, propylene glycol, as well as diacetone alcohol.

Dyeing is carried out in conventional manner, for example with metal complex dyes or also with anthraquinone dyes or azo dyes. The metal complex dyes used are the known types, especially the 1:2 chromium or 1:2 cobalt complexes of monoazo or diazo or azomethine dyes which are copiously described in the literature. In addition to these dyes, it is of course also possible to use dyes of other classes, for example disperse dyes or also vat dyes.

The foam forming compositions can also be used for fibre materials which have been whitened with fluorescent whitening agents. Depending on the substrate, anionic or cationic as well as water-dispersible fluorescent whitening agents are used. The fluorescent whitening agents may belong to the coumarin, oxazine, naphthalimide, stilbene, styryl, pyrazine, pyrazoline, triazo-

lyl, benzofuranlyl, benzoxazolyl, bis(benzoxazolyl), thiophenebis(benzoxazolyl) or benzimidazolyl series.

The foamed aqueous composition can be prepared by simple stirring of the individual components (a), (b) and additional optional components (c) and (d) in water.

The foamed aqueous composition conveniently comprises, based on said composition, 2 to 20 percent by weight, preferably 6 to 14 percent by weight of component (a), 0.5 to 10 percent by weight, preferably 1 to 4 percent by weight of component (b), 0 to 2 percent by weight, preferably 0 to 1 percent by weight of component (c), 0 to 5 percent by weight, preferably 0 to 1.5 percent by weight of component (d), and water to make up 100%.

The amounts in which the foamed composition is added to the treatment liquor range from 1 to 30 g, preferably from 4 to 20 g, per liter of treatment liquor, depending on the dyeing or finishing process. In these amounts, the copper content per g of polyamide fibre material is from 5 to 200 μ g.

Polyamide material will be understood as meaning synthetic polyamide such as polyamide 6, polyamide 66 or polyamide 12. In addition to pure polyamide fibres, blends of polyurethane and polyamide are also suitable, for example polyamide/polyurethane blends in the ratio of 70:30. In principle, the pure or blended material can be in any form of presentation, for example fibres, yarn, woven fabrics, pile fabrics or knitted goods.

Pile fabrics made from polyamide or polyamide/polyurethane blends are preferred.

The process of this invention is especially suitable for treating polyamide material which is exposed to the action of light and heat and is used as car upholstery or carpeting.

The aftertreatment and dye liquors can also contain conventional auxiliaries, suitably electrolytes such as salts, for example sodium sulfate, ammonium sulfate, sodium or ammonium phosphates or polyphosphates, ammonium acetate or sodium acetate and/or acids such as mineral acids, for example sulfuric acid or phosphoric acid, or organic acids, preferably lower aliphatic carboxylic acids such as formic acid, acetic acid or oxalic acid. The acids are added in particular to adjust the pH of the liquors of this invention.

Depending on the substrate to be treated, the pH is generally in the range from 4 to 8.

Depending on the desired effect, the aftertreatment and dye liquors additionally contain further auxiliaries or modifiers such as catalysts, ureas, oxidising agents, retardants, dispersants, stabilisers or emulsifiers.

The aqueous composition for carrying out the process also constitutes an object of the present invention. The composition comprises

- a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes
- an anionic or nonionic surfactant or a mixture of said surfactants, and, as optional components,
- a salt of a hydrolysed polymaleic anhydride, and
- a polar organic solvent.

A preferred embodiment of the composition of the invention comprises

- a copper complex of formula (2),
- a mixture of a sulfated polyadduct of a fatty alcohol with ethylene oxide containing 8 to 18 carbon atoms in the alcohol moiety and 2 to 4 ethylene oxide units,

or the alkali metal salt thereof, and, as optional components,

- the sodium or ammonium salt of a hydrolysed polymaleic anhydride having a molecular weight of 300 to 500, and
- ethylene or propylene glycol and diacetone alcohol.

The foams are preferably produced by mechanical means using impellers, dynamic or static mixers or also special foam pumps, with which latter the foams can also be produced continuously. In the process of this invention, blow ratios, i.e. volume ratios of foamed to unfoamed composition, of 1:6 to 1:12, preferably 1:8 to 1:10, have been found suitable.

The foams used in the practice of this invention are stable over a considerable period of time and do not collapse immediately when applied to the substrate. The foams used in the practice of this invention preferably have half-lives of 2 to 10 minutes. The bubbles in the foams have diameters from ca. 1 to 100 μ .

The foams can be applied uniformly to the fibre materials by a wide variety of techniques. Exemplary of some techniques are: vacuum penetration, rolling on, rolling on/suction, doctor coating with fixed blades or roll coating (on one or both sides), padding, blowing in, compressing, passing the textile substrate through a chamber which is continuously charged with and in which foam is under a certain pressure. These procedures cause the foam to collapse, i.e. the foam decomposes and wets the textile material.

The application of the foam is normally made at room temperature, i.e., in the temperature range from 15° to 30° C. The add-on of foam is normally 10 to 100 percent by weight, preferably 30 to 80 percent by weight, based on the treated material.

For the photochemical stabilisation of the dyed textiles, a treatment liquor is foamed and the foam is applied continuously by means of an applicator roll to the face of the fabric from a foam container, preferably with adjustable doctor blade. If desired, the application, of foam can be repeated on the back of the fabric. When applying foam to the face and back of the fabric, it is not necessary to effect an intermediate drying between the applications to the face and to the back. It is also possible to apply different treatment liquors to the face and to the back of the fabric.

Another means of applying the foam consists in padding the substrate with a padding liquor containing the foamed composition. Impregnation is preferably made to a liquor pick-up of 40 to 100 percent by weight.

After the foam application, the textile material is dried in the temperature range from 100° to 160° C.

In the following Examples, percentages are by weight, unless otherwise stated.

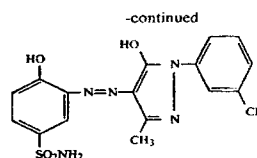
EXAMPLE I

5 carpet samples having a weight of 500 g/m² are prepared. The carpets are wetted on a winchbeck for 5 minutes at 20° C. in an aqueous liquor which contains, per liter, 2% of a nonionic levelling agent based on alkylamine polyglycol ether. The pH is 7. To the liquor is then added the following combination of dyes:

0.22% of the dye of formula

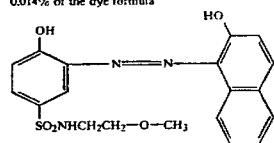
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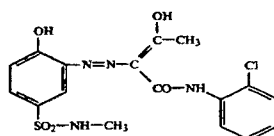
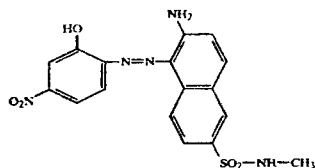
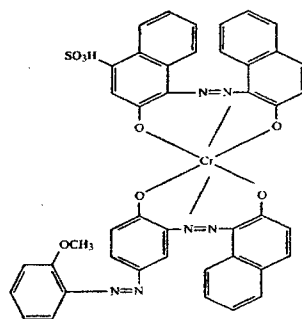


(1:2 Co complex)

0.014% of the dye formula



and 0.095% of a mixture of dyes of formulae



After addition of the dye combination, treatment is continued for 5 minutes at the same temperature. The temperature is then raised over 45 minutes to 98° C. and dyeing is continued for 45 minutes at this temperature.

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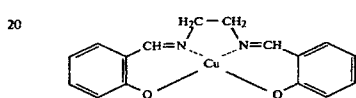
The samples are removed from the dyebath and rinsed with cold water.

(101) A foam is prepared in a foaming apparatus from a liquor comprising

- 5 a) 1 g/l of a composition consisting of
2.0% of 50% NaOH
5.0% of a 50% aqueous polymaleic acid
15.0% of coconut fatty acid diethanolamide
25.0% lauryl triglycol ether sulfate
9.0% of diacetone alcohol and
44% of water

(102) as well as

- 15 b) 16 g/l of a composition consisting of
10.0% of the copper complex of formula



- (103a) 4.3% of sodium sulfate
2.5% of an ethylene oxide/propylene oxide block polymer
10% of Mg-Al silicate
0.75% of 1,2-propylene glycol
0.3% of a polysaccharide and
81.15% of water.

35 The foam has a blow ratio of 1:9 and a half-life of 5 minutes.

The individual carpet samples are treated as follows:
Sample 1: The carpet is treated at 140° C. after dyeing. No aftertreatment is carried out.

40 Sample 2: The carpet sample is impregnated on a pad with the foaming liquor to a pick-up of 50% and then dried at 140° C.

45 Sample 3: The foam is applied continuously with a coating knife for adjusting the desired foam thickness to the pile side of the carpet via an applicator roll using a carriage. The pick-up is 50%. The running speed is 12 m/min. The height of the foam is 10 mm. The foam add-on is 50%. The carpet is subsequently dried at 140° C.

50 Sample 4: The procedure is carried as for sample 3, except that the pick-up is 100%.

EXAMPLES 2-4

(103b) 55 In these examples the concentration of the copper complex compound of formula (104) is varied.

EXAMPLE 2

60 A carpet sample (=sample 5) having a weight of 500 g/m² is wetted, dyed and rinsed with cold water as described in Example 1. The sample is aftertreated as described for sample 2, except that 12 g/l of composition b) is used.

EXAMPLE 3

The procedure of Example 2 is repeated, except that 8 g/l of composition b) is used (=sample 6).

17

EXAMPLE 4

The procedure of Example 2 is repeated, except that 4 g/l of the compound of composition b) is used (=sample 7).

The lightfastness of the dyed and aftertreated carpet samples is determined in accordance with DIN 75.202 (FAKRA). The results are reported in Table 1.

TABLE 1

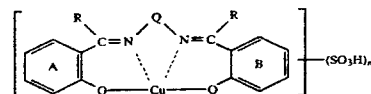
sample	Exposure: DIN 75.202 (FAKRA)		
	1 × Fakra (=72 h)	2 × Fakra (=144 h)	3 × Fakra (=216 h)
sample 1	4-5	3H ⁺	2H
sample 2	5	-5	4-5
sample 3	5	5	-5
sample 4	5	5	-5
sample 5	4-5	4	+3-4
sample 6	4-5	4	3-4
sample 7	4-5	4	-3-4

The results show that the lightfastness properties of the dyeings which are treated with the composition of the invention are markedly better than comparison dyeings without aftertreatment (sample 1).

What is claimed is:

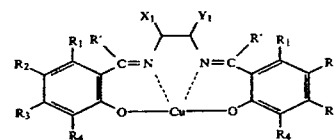
1. A process for the photochemical stabilisation of dyed polyamide fibre materials, which comprises treating the dyed material with a foamed aqueous composition which contains at least (a) a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes.

2. A process according to claim 1, wherein component (a) is a compound of formula



in which R is hydrogen or a substituted or unsubstituted alkyl or aryl radical, Q is a substituted or unsubstituted alkylene, cycloalkylene or arylene radical and n is 0, 1, 2 or 3.

3. A process according to claim 2, wherein component (a) is a bisazomethine complex of formula



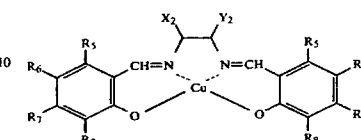
in which R' is hydrogen, R₁, R₂, R₃ and R₄ are each hydrogen, halogen, hydroxyl, hydroxyalkyl, alkyl, alkoxy, alkoxyalkoxy, alkoxyalkoxyalkoxy, carboxymethoxy, alkylamino, dialkylamino, -SO₂NH₂, -SO₂NHR₀ or -SO₂N(R₀)₂, R₀ being alkyl or alkoxy-alkyl, and alkyl or alkoxy each being understood as groups having 1-4 carbon atoms, or R₁ and R₂ or R₂ and R₃ or R₃ and R₄, together with the carbon atoms to which they are linked, form a benzene radical, and X₁ and Y₁ are hydrogen, C₁-C₄alkyl or an aromatic radical

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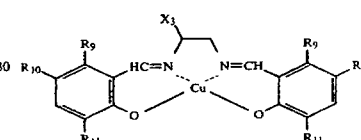
or X₁ and Y₁ form together with the carbon atom to which they are linked a cycloaliphatic radical of 5-7 carbon atoms.

4. A process according to claim 3, wherein component (a) is copper complex compound of the formula



wherein R₅-R₈ are each and independently from each other hydrogen, hydroxyl, chlorine, bromine methyl, tert-butyl, methoxy, methoxyethoxy, ethoxyethoxyethoxy or diethylamino, X₂ hydrogen, methyl, ethyl or phenyl and Y₂ hydrogen or R₅ and R₆ together form a fused benzene ring or X₂ and Y₂ together form a cyclohexylene radical.

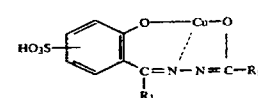
5. A process according to claim 4, wherein component (a) is copper complex compound of the formula



wherein R₉, R₁₀ and R₁₁ are each independently of one another hydrogen, chloro, bromo, methyl or methoxy, or wherein R₉ and R₁₀ together form a fused benzene ring, and X₃ is hydrogen, methyl, ethyl or phenyl.

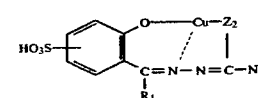
6. A process according to claim 5, wherein component (a) is a compound of formula (4), wherein R₉, R₁₀, R₁₁ and X₃ are hydrogen.

7. A process according to claim 1, wherein component (a) is a copper complex of the formula



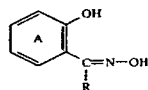
in which R₁ and R₁₂ independently of one another are hydrogen or a substituted or unsubstituted alkyl or aryl radical.

8. A process according to claim 1, wherein component (a) is a copper complex of the formula



in which R₁ is as defined under the formula (5) and Z₂ is oxygen or sulfur.

9. A process according to claim 1, wherein component (a) is a copper complex of the formula



wherein R is hydrogen, hydroxy, alkyl or cycloalkyl, and in which the ring A is unsubstituted or further substituted.

10. A process according to claim 1, wherein the foamed aqueous composition additionally comprises an anionic or nonionic surfactant, or a mixture thereof, as component (b), and a salt of a hydrolysed polymaleic anhydride as optional component (c), and a polar organic solvent as optional component (d).

11. A process according to claim 10, wherein component (b) is a combination of the components:

- (I) acid esters or their salts of a polyadduct of 2 to 15 mol of ethylene oxide with 1 mol of a fatty alcohol containing 8 to 22 carbon atoms or with 1 mol of an alkylphenol containing 4 to 12 carbon atoms in the alkyl moiety,
- (II) alkylphenylsulfonates containing 8 to 18 carbon atoms in the alkyl moiety,
- (III) sulfonated 1-benzyl-2-alkylbenzimidazoles containing 8 to 22 carbon atoms in the alkyl moiety,
- (IV) polyadducts of 2 to 15 mol of ethylene oxide with 1 mol of a fatty alcohol or fatty acid, each containing 8 to 22 carbon atoms, or with 1 mol of alkylphenol containing a total of 4 to 12 carbon atoms in the alkyl moiety,
- (V) a fatty alcohol or a mono-, di- or triethoxylated fatty alcohol containing 8 to 22 carbon atoms in the fatty alcohol radical, or
- (VI) a fatty acid diethanolamide containing 8 to 12 carbon atoms in the fatty acid radical.

12. A process according to claim 1, wherein component (a) is a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes, and component (b) is a combination of components (I), (II), (III), (IV), (V) and (VI).

13. A process according to claim 1, wherein component (a) is a copper complex of formula (2), and component (b) is a combination of components (I), (II), (III), (IV), (V) and (VI).

14. A process according to any one of claim 10, wherein component (b) is a mixture of a sulfated polyadduct of a fatty alcohol and ethylene oxide containing 8 to 18 carbon atoms in the alcohol moiety and 2 to 4 ethylene oxide units, or the alkali metal salt thereof,

and a fatty acid diethanolamide containing 8 to 18 carbon atoms in the fatty acid radical.

15. A process according to claim 10, wherein component (b) is a mixture of sodium lauryl triglycol ether sulfate and a fatty acid diethanolamine containing 8 to 18 carbon atoms in the fatty acid radical.

16. A process according to claim 10, wherein optional component (c) is a sodium or ammonium salt of a hydrolysed polymaleic anhydride having a molecular weight of 300 to 5000.

17. A process according to claim 10, wherein optional component (d) is ethylene or propylene glycol and diacetone alcohol.

18. A process according to claim 1, wherein the foamed aqueous composition comprises

- 2 to 20 percent by weight of component (a),
- 0.5 to 10 percent by weight of component (b),
- 0 to 2 percent by weight of component (c),
- 0 to 5 percent by weight of component (d), and
- water to make up 100%.

19. A process according to claim 1, wherein the blow ratio is 1:6 bis 1:12.

20. A process according to claim 1, which comprises applying the foamed treatment liquor continuously via an applicator roll to the dyed textile material and drying the treated material after possible decomposition of the foam.

21. A process according to claim 1, which comprises padding the dyed textile material with the treatment liquor.

22. An aqueous composition comprising

- (a) a non-dyeing copper complex of bisazomethines, acylhydrazones, semicarbazones or thiosemicarbazones of aromatic aldehydes or ketones or oximes
- (b) an anionic or nonionic surfactant or a mixture of said surfactants, and, as optional components,
- (c) a salt of a hydrolysed polymaleic anhydride, and
- (d) a polar organic solvent.

23. A composition according to claim 22, which comprises

- (a) a copper complex of formula (2),
- (b) a mixture of a sulfated polyadduct of a fatty alcohol with ethylene oxide containing 8 to 18 carbon atoms in the alcohol moiety and 2 to 4 ethylene oxide units, or the alkali metal salt thereof, and, as optional components,
- (c) the sodium or ammonium salt of a hydrolysed polymaleic anhydride having a molecular weight of 300 to 5000, and
- (d) ethylene or propylene glycol and diacetone alcohol.

24. Dyed polyamide textile material which is photochemically stabilised by a process as claimed in claim 1.