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<p>(54) Title: DEACIDIFICATION OF CELLULOSE BASED MATERIALS USING HYDROFLUOROETHER CARRIERS</p>		
<p>(57) Abstract</p> <p>An improved method of deacidifying books, imaged paper and other imaged materials having a cellulose base wherein, for a sufficient time to raise the pH of the materials, the materials are treated with alkaline particles of a basic metal oxide, hydroxide or salt dispersed in a hydrofluoroether carrier, alone, or in combination with a perfluorinated carrier. A surfactant is added.</p>		

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TITLE: DEACIDIFICATION OF CELLULOSE BASED MATERIALS
USING HYDROFLUOROETHER CARRIERS

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BACKGROUND OF THE INVENTION:

The deterioration of paper, books and newspapers is
10 well-known and of growing concern to librarians and
archivists throughout the world. The causes of paper
deterioration are numerous and include inherent acidity,
photodegradation, oxidation, and even microbiological attack
under certain conditions. These factors combined with
15 initial paper quality have severely reduced the permanence of
library and archival collections. It is becoming generally
accepted that the most insidious problem is the acidity of
most book paper produced in the last one hundred years.

The demand for large amounts of printing paper over
20 the last century led to the introduction of pulp fiber
produced from wood by chemical or mechanical means. However,
paper made from untreated wood pulp is too absorbent to allow
sharp image imprint. Therefore, chemicals have to be added
to the wood fibers during processing. These additives allow
25 the paper to accept inks and dyes and increase paper opacity.
Unfortunately, most of these chemicals are either acidic or
are deposited by acidic mechanisms which initiate the slow,

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but relentless acidic deterioration of paper. Other contributions to the acidification of paper are supplied by man through industrial emissions of sulfur and nitrogen and carbon oxides or by natural processes such as sea salt spray.

5 Even books or paper of neutral and alkaline characters are not immune. As neighboring papers of acidic nature degrade, volatile acids are produced which either diffuse through adjoining books or permeate the atmosphere and may ultimately acidify even the "safe or stable" books.

10 In order to arrest this acidic degradation, paper materials must be deacidified and provided with an alkaline reserve or buffer to retard a return to an acidic state. There are several known processes for deacidifying paper whether bound or unbound. Numbering among these are
15 processes using volatile metal alkyls, e.g. U.S. Patent Nos. 3,969,549, and 4,051,276, and volatile amines e.g. U.S. Patent Nos. 3,472,611, 3,771,958 and 3,703,353. U.S. Patent No. 3,676,182 describes the treatment of cellulosic materials with alkali and alkaline earth bicarbonates, carbonates, and
20 hydroxides in a halogenated hydrocarbon solvent or lower aliphatic hydrocarbon such as n-butane with an optional plasticizing agent such as ethylene glycol. U.S. Patent No. 3,676,055 to Smith describes a nonaqueous deacidification solution for treating cellulosic materials comprising 1000 cc
25 of 7 percent magnesium methoxide in methanol and in addition 20 pounds (9.0 kg) of dichlorodifluoromethane (Freon 22). Canadian Patent No. 911,110 to Smith describes a deacidification solution of a 7% magnesium methoxide solution in methanol (10 parts) and a halogenated solvent or solvents
30 (90 parts): and states that a magnesium alkoxide reacts with

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water in paper to form a mildly alkaline milk of magnesia, being magnesium hydroxide. Improved results are reported with the use of the halogenated hydrocarbon solvents.

Unfortunately, all of these processes suffer from one or more of a number of drawbacks that have prevented their wide-spread acceptance. These drawbacks include high cost, toxicity, complexity of treatment, residual odor, deleterious effects on certain types of paper and inks, lack of an alkaline reserve, and the necessity of drying the book or paper to very low moisture contents before treatment.

Kundrot, U.S. Patent No. 4,522,843, provided a solution to the problems experienced with prior art systems. The method of the Kundrot patent utilizes a dispersion of alkaline particles of a basic metal oxide, hydroxide or salt, such as magnesium oxide, in a gas or liquid dispersant. The MgO, when converted to Mg(OH)₂, according to the reaction $MgO + H_2O \rightarrow Mg(OH)_2$ effectively neutralizes the initial acidity in the paper and provides an adequate alkaline reserve to counter future re-acidification. The deacidification reactions occur later (a period of days) and are typically described as $Mg(OH)_2 + H_2O_4 \rightarrow MgSO_4 + 2 H_2O$. The liquid dispersant or carrier, described in the Kundrot patent is an inert halogenated hydrocarbon. It does not take part in the deacidification, but serves to carry the particles to the fabric of the paper. In several embodiments described, the halogenated hydrocarbons are Freons, or chlorofluorocarbons (CFC). CFC's have since been found to harm public health and the environment by depleting ozone in the upper atmosphere. Manufacturers of CFC's presently place limits on the amounts

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they will sell to any one purchaser and are phasing out production of CFC's entirely.

A replacement for the CFC carrier in the method of deacidifying books and other cellulose based materials described in the Kundrot patent was described in Leiner et al., U.S. Patent No. 5,409,736. The Leiner patent replaced the CFC's of the Kundrot patent with perfluorinated carriers, such as perfluoropolyoxy ether and perfluoromorpholine. Unlike CFC's, perfluorocarbons are not known to cause damage to the ozone layer. However, perfluorocarbons are classified as greenhouse gases because they decompose slowly and trap heat in the atmosphere.

SUMMARY OF THE INVENTION:

The present invention provides an improvement in a method for deacidifying cellulose based materials, such as books, magazines, newspapers, maps, documents, photographs and postcards, facsimile paper, folders, imaged paper and the like. The method involves generally treating the cellulose based materials with alkaline particles of a basic metal selected from the group consisting of oxides, hydroxide and salts, dispersed in a carrier liquid or similar dispersion medium, in an amount and for a time sufficient to pass the alkaline particles into the interstices of the materials and increase the pH of the materials. The improvement comprises dispersing the alkaline particles in an inert medium comprised of a hydrofluoroether carrier and a surfactant. Optionally, the carrier may include combinations of hydrofluoroether and a perfluorinated compound.

The hydrofluoroether carrier of the present invention does not damage the cellulose based materials by

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discoloring pages or leather bindings and covers, nor does it cause inks to run or fade or weaken bindings. The new carrier has a relatively short lived atmospheric life time, disassociating into components in few years. The new carrier
5 has an ozone depletion potential of zero and is not classified as a greenhouse gas. Therefore, it is ecologically preferable to the CFC's used in the past.

The hydrofluoroether carriers have been found to provide a better dispersion of the alkaline particles with
10 less surfactant than the CFC or the perfluorinated carriers.

BRIEF DESCRIPTION OF THE FIGURE:

FIG. 1 is a graph showing the comparison between the settling rate for samples of alkaline particles dispersed in hydrofluoroether and that of samples of alkaline particles
15 dispersed in a perfluorinated compound.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:

The cellulosic materials can be treated with any suitable basic metal oxide, hydroxide or salt as described in U.S. Patent No. 4,522,843 to Kundrot, which is hereby
20 incorporated herein by reference. Suitable materials, according to the Kundrot patent, are the oxides, hydroxides, carbonates and bicarbonates of the Group I and II metals of the Periodic table and zinc. Preferred are the materials in which the cation is magnesium, zinc, sodium, potassium, or
25 calcium. Particularly preferred are the relatively non-toxic oxides, carbonates and bicarbonates of magnesium and zinc and the hydroxides of sodium, potassium and calcium. Representative examples include magnesium oxide, magnesium carbonate, magnesium bicarbonate, zinc carbonate, zinc

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bicarbonate, zinc oxide, sodium hydroxide, potassium hydroxide and calcium hydroxide. Magnesium oxide is most preferred. The predominate particle size (95-99%) is preferably between 0.05 and 2.0 micron. Typical surface areas are between 50 and 200 m²/g BET, preferably about 170-180 m²/g.

The particles can be formed by burning the elemental metal and collecting the smoke, attrition of the preformed oxides or calcination of the elemental salts. For example, basic magnesium carbonate can be calcined at 450°C-550°C. to produce a polydisperse high activity magnesium oxide with an average particle size of 0.4 microns and a predominant particle size between 0.1 and 1.0 micron. The smaller particles can be filtered out.

The particles can be applied in the paper making process or to the finished paper by immersing the paper in a suspension of the non-aqueous inert deacidifying fluid. Inert as used herein means that there is a very low interaction, and preferably no interaction, between the fluid medium and inks, dyes, bindings, cover materials and the like in the cellulose based materials. The inert fluid medium of the present invention is a hydrofluoroether carrier and a surfactant that will disperse the alkaline particles in the carrier.

Optionally, the carrier may be comprised of a combination of hydrofluoroether and perfluorinated compounds. Hydrofluoroether is miscible in all proportions with perfluorinated compounds so the carriers blend readily. The volatility of the carrier medium can be adjusted by adding varying amounts of perfluorinated compounds to achieve a

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desired volatility. Perfluorohexane is more volatile than perfluoroheptane, so would be preferred in combination with hydrofluoroether where a greater volatility is desired.

It is believed that samples representative of the entire range of papers used in the United States were included in testing of the hydrofluoroether carrier; papers such as those found in hard cover and soft cover books, encyclopedias, periodicals, newspapers, magazines, comic books and other documents. In addition, tests were run on a variety of bindings including backrams, leathers, synthetic leathers and polymers.

While any suitable known surfactant may be used, it is important that the surfactant not cause damage or leave any telltale odor. It must also be soluble in hydrofluoroether. A preferred surfactant is perfluoropolyoxyether alkanolic acid. In prior carrier media, the surfactant is important for the proper dispersion of the alkaline particles throughout the carrier. It was soon discovered, however, that when hydrofluoroether is used as the dispersant for the alkaline particle, a better dispersion is achieved with much less surfactant than is used in the prior systems. Tests were done to compare the settling times for dispersions wherein perfluorinated carriers or hydrofluoroether carriers were used. The values set forth in the Table were obtained by measurements using a light transmission method. The values are reported in Nephelometric Turbidity Units (NTU). As the NTU value drops, more light is transmitted through the sample, meaning that more of the dispersed phase, in this case alkaline particles, have settled out of the dispersion. Settling rate is

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directly correlated to the average particle size in the dispersion. The perfluorinated carrier tested was perfluoroheptane, identified as PF5070 in the Table. The hydrofluoroether tested was nonafluoromethoxybutane, identified as HFE7100 in the Table. The surfactant used in the testing was perfluoropolyoxyether alcanoic acid (Fomblin® monoacid). The results are set forth in Table 1.

Table 1
DISPERSION STUDIES

NTU	Elapsed Minutes	DROP	CUMUL	%LOSS	Regression Output:
HFE 7100 MgO .4g/l Surfactant .1g/l					
1196	0	0	0	0	Constant 3.082244
1122	15	74	74	6.187291	Std Err of Y Est 2.1224
1046	30	76	150	12.54181	R Squared 0.962225
1071	45	-25	125	10.45151	No. of Observations 11
1001	60	70	195	16.30435	Degrees of Freedom 9
968	75	33	228	19.06355	
938	90	30	258	21.57191	
890	105	48	306	25.58528	X Coefficient(s) 0.204267
837	120	53	359	30.01672	Std Err of Coef. 0.013491
841	135	-4	355	29.68227	
825	150	16	371	31.02007	
PFE 5070 MgO .4g/l Surfactant .1g/l					
923	0	0	0	0	Regression Output:
816	15	107	107	11.59263	Constant 7.199842
749	30	67	174	18.85157	Std Err of Y Est 5.258791
678	45	71	245	26.54388	R Squared 0.942268

576	60	102	347	37.5948	No. of Observations	11
566	75	10	357	38.67822	Degrees of Freedom	9
447	90	119	476	51.57096		
421	105	26	502	54.38787	X Coefficient(s)	0.405135
409	120	12	514	55.68797	Std Err of Coef.	0.033427
388	135	21	535	57.96316		
364	150	24	559	60.56338		

NTU	Elapsed Minutes	DROP	CUMUL	%LOSS	Regression Output:
HFE 7100 MgO .4g/l Surfactant .075g/l					
1037	0	0	0	0	Constant 2.945552
981	15	56	56	5.400193	Std Err of Y Est 2.01327
964	30	17	73	7.039537	R Squared 0.973994
905	45	59	132	12.72903	No. of Observations 11
863	60	42	174	16.77917	Degrees of Freedom 9
818	80	45	219	21.11861	X Coefficient(s) 0.194234
803	95	15	234	22.56509	Std Err of Coef. 0.01058
769	110	34	268	25.84378	
738	135	31	299	28.83317	
687	160	51	350	33.75121	
663	185	24	374	36.06557	
HFE 7100 MgO .4g/l Surfactant .025g/l					
911	0	0	0	0	Constant 3.205269
887	15	24	24	2.634468	Std Err of Y Est 2.583309
835	30	52	76	8.342481	R Squared 0.963476
768	45	67	143	15.69704	No. of Observations 14
735	60	33	176	19.31943	Degrees of Freedom 12
720	75	15	191	20.96597	

717	90	3	194	21.29528		
697	105	20	214	23.49067	X Coefficient(s)	0.20315
653	120	44'	258	28.32053	Std Err of Coef.	0.011418
608	135	45	303	33.26015		
601	150	7	310	34.02854		
570	165	31	341	37.43139		
571	180	-1	340	37.32162		
546	195	25	365	40.06586		

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The data from Table 1 is presented in FIG. 1. From the values shown, it can be seen that the settling rate for hydrofluoroether 7100 (HFE7100) is about half that of the perfluorinated compound tested (PF5070). From Stokes law for the free-settling velocity of spherical particles at low Reynolds Number, this corresponds to a decrease in effective particle size of approximately 50%. In gravitational sedimentation methods, particle size is determined from settling velocity. The equation relating particle size to

10 settling velocity is known as Stokes Law: $d_{st} = \sqrt{\frac{18\eta u}{(p_s - p_f)g}}$ where d_{st} is the Stokes diameter, η is viscosity, u is the particle settling velocity under gravity, p_s is the particle density, p_f is the fluid density and g is the acceleration due to gravity. Therefore, Stokes diameter is directly proportional to the square root of the settling velocity and inversely proportional to the difference in particle and fluid density. See, Perry's Chemical Engineering Handbook, 20-7 (7th ed).

It can also be seen from the results in Table 1, that a decrease in the amount of surfactant by a factor of four has no effect on the settling rate of MgO in HFE7100.

As provided in the Kundrot patent, a suitable carrier for a liquid suspension of particles is preferably inert and possesses a high enough vapor pressure to allow its removal from the paper following treatment. The boiling point for the hydrofluoroethers are within the range of 40°C-100°C. The boiling point for the preferred carrier is 60°C.

An odor test was conducted by fanning books, magazines and other cellulose based material being evaluated after treatment using hydrofluoroether and Fomblin® monoacid

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as the surfactant and recording the first impression on a scale of 0 to 5, from no odor at all to an overpowering odor. No odor was detected in dry books. Fomblin® monoacid is completely soluble in HFE 7100.

5 In use, a bath of an inert carrier and its suitable associated surfactant is prepared by adding to the carrier an amount of the appropriate surfactant, preferably 1×10^{-3} wt %. The alkaline particles are then added and dispersed throughout the carrier-surfactant medium.

10 The amount of surfactant and alkaline material will depend in part on the length of treatment and the amount of deposition desired. The carrier is present in excess amounts, sufficient to immerse the quantity of materials being treated. Generally, however, the concentration of
15 alkaline material will be between about 0.01 and about 0.6 weight percent. A most preferred range for the basic material particles is between about 0.01% and about 0.2%, the preferred range for the surfactant is between about 6.25×10^{-4} and 3.74×10^{-2} . The preferred alkaline particles, MgO,
20 are generally present in a dispersion maintained at approximately 0.3 - 6.0 g/L MgO based on the volume of the carrier.

 The suspension of alkaline particles in the hydrofluoroether carrier and surfactant is preferably sprayed
25 onto the pages of a book or other document. Alternatively, the cellulose based materials may be immersed into a bath, and preferably moved as described in U.S. Patent No. 5,422,147 and in US patent application serial number 08/586,252 filed January 16, 1996 both of which are hereby

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incorporated herein by reference. The movement is preferably continued for 10-30 minutes at room temperature.

The suspension permeates the fibers of the paper leaving alkaline particles behind when the carrier and surfactant medium are evaporated. The pH of the paper is thereby raised and an alkaline reserve of at least 300 milliequivalents reserve per kilogram of paper typically remains in the fiber of the paper. Paper treated with the improved process of the present invention typically show a pH value ranging from 7.5 to 9.5.

The following example demonstrates that the pH of test strips of paper was raised using the improved process of the present invention.

15

Examples

Example 1

Twenty-five percent (25%) rag bond paper having an initial pH of 5.5 and an initial alkaline reserve of 0% was dipped in a dispersion of 0.3g/l MgO, 0.075 g/l Fomblin® in HFE 7100 for 15 minutes at room temperature. Following drying, the pH of the paper was 9.9 and the alkaline reserve was 1.75% (reported as weight percent calcium carbonate equivalent).

25 Example 2

Experiment 1 was repeated using a dispersion of 0.6 g/l MgO and 0.15 g/l Fomblin® in HFE 7100. The pH of the paper rose to 9.8 and the alkaline reserve rose to 2.35% (wt % calcium carbonate equivalent).

Example 3

Experiment 1 was repeated using a dispersion of 0.3g/l MgO, 0.3 g/l ZnO, 0.15 g/l Fomblin® in HFE7100. The treated paper had a pH of 9.4 and an alkaline reserve of
5 1.65% (wt % calcium carbonate equivalent).

Example 4

Experiment 1 was repeated, dipping the bond paper into a dispersion of 4.0 g/l MgO and 1.2 g/l Fomblin® in HFE 7100. The treated paper had a pH of 9.6 and an alkaline
10 reserve of 1.98% (wt % calcium carbonate equivalent).

Example 5

A dispersion of 4.0 g/l MgO, 1.2 g/l Fomblin® in HFE 7100 was sprayed evenly onto the entire surface of both sides of a standard 8-1/2 x 11 inch sheet of paper having a
15 pH of 5.5 and an alkaline reserve of zero, at a rate of 90 ml/min. for 2.5 seconds per side. Approximately 7.5 ml dispersion was applied. The treated paper had a pH of 9.5 and an alkaline reserve of 1.6% (wt % calcium carbonate equivalent).

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What we claim is:

1. In a method of deacidifying cellulose based materials which includes the step of treating said material with suitable alkaline particles of a basic metal selected from
5 the group consisting of oxides, hydroxides and salts dispersed in a liquid carrier in an amount and for a time sufficient to pass into the interstices of the cellulose based materials and increase the pH thereof, the improvement comprising:
10 dispersing said particles of metal in an inert medium comprised of a carrier and an associated surfactant, the carrier consisting of a hydrofluoroether.
2. The improvement of claim 1 wherein the surfactant is perfluoropolyoxyether alkanolic acid.
- 15 3. The improvement of claim 1 wherein the surfactant is present in amounts between 6.25×10^{-4} and 3.84×10^{-2} weight percent.
4. The improvement of claim 1 wherein the alkaline particles are present in amounts between about 0.01 and 0.6
20 weight percent.
5. The improvement of claim 1 wherein the carrier is additionally comprised of an amount of a perfluorinated compounds.

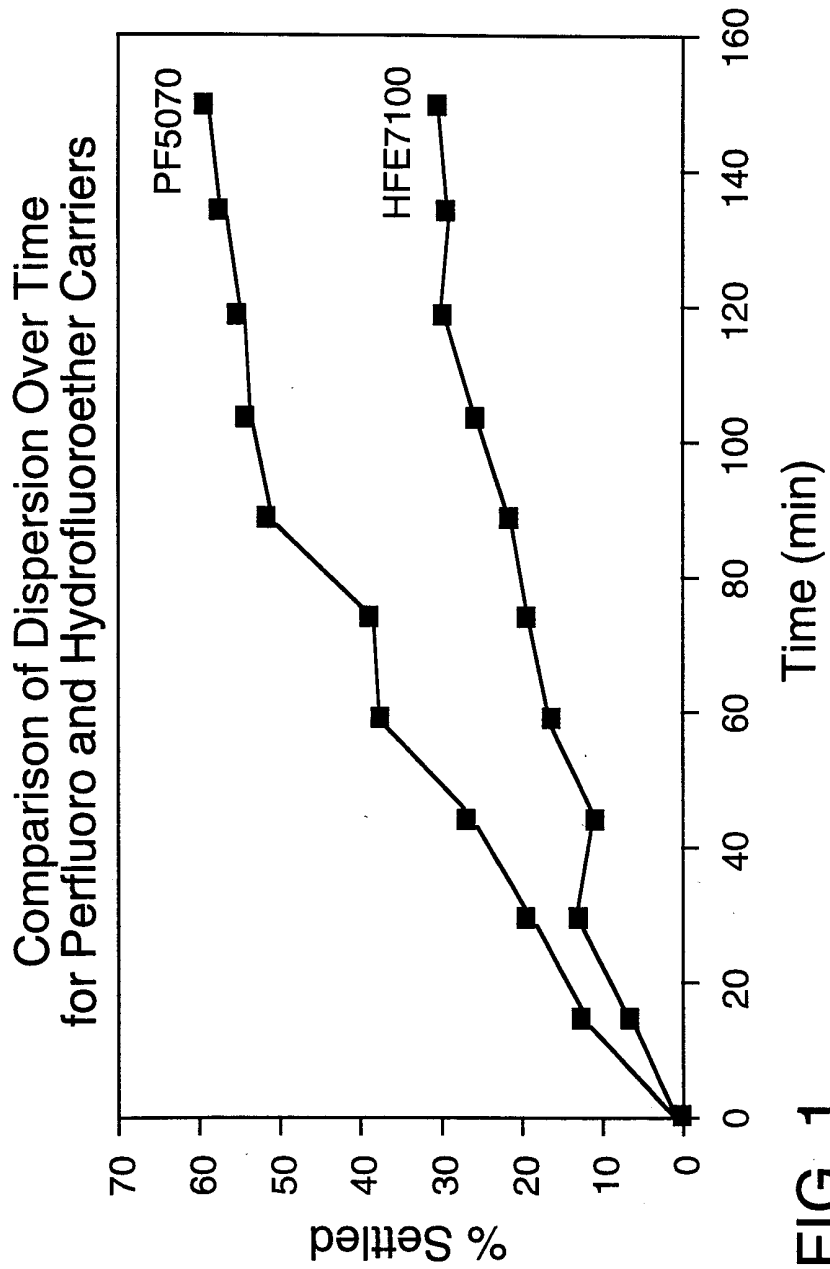


FIG. 1

INTERNATIONAL SEARCH REPORT

Intern: al Application No
PCT/US 99/06596

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 D21H25/18 //D21H17:06, D21H17:11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 409 736 A (LEINER LEE H ET AL) 25 April 1995 cited in the application Examples see column 7, line 66 - column 8, line 15 see claims 4,5 ---	1-5
X	WO 97 26409 A (PRESERVATION TECH INC) 24 July 1997 see page 24, line 4 - line 24 --- -/--	1,2,5

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search 22 June 1999	Date of mailing of the international search report 01/07/1999
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INTERNATIONAL SEARCH REPORT

Intern: al Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9817 Derwent Publications Ltd., London, GB; Class E33, AN 98-189876 XP002106837 & JP 10 046497 A (KATO H) , 17 February 1998 see abstract <p style="text-align: center;">---</p>	1
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...ormation on patent family members

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