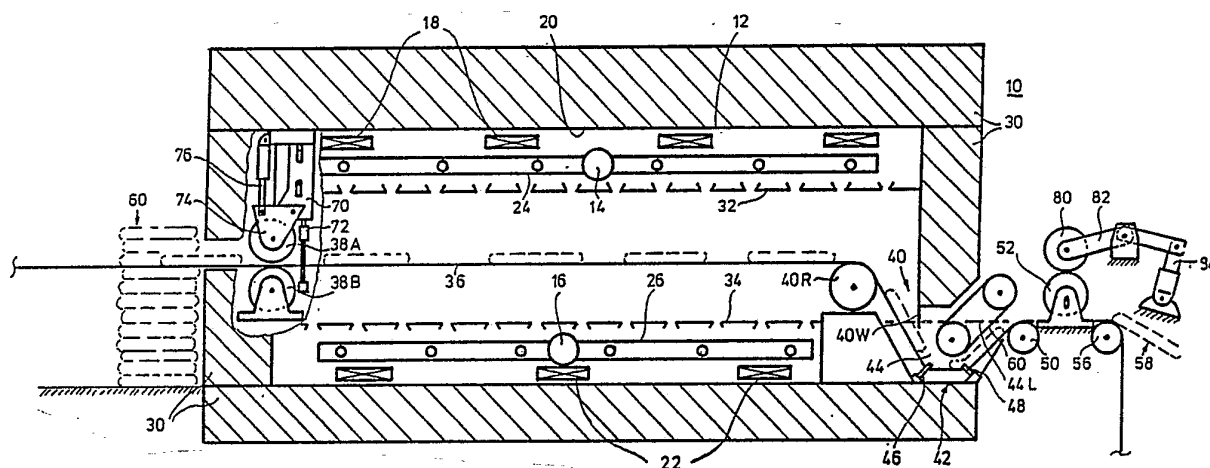




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : C14C 15/00	A1	(11) International Publication Number: WO 89/ 07155 (43) International Publication Date: 10 August 1989 (10.08.89)
(21) International Application Number: PCT/EP89/00088 (22) International Filing Date: 2 February 1989 (02.02.89) (31) Priority Application Number: 8802745 (32) Priority Date: 6 February 1988 (06.02.88) (33) Priority Country: GB (71) Applicant (for all designated States except US): DYNAVAC MASCHINENBAU GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG [DE/DE]; Industriestr. 32, D-6252 Diez (DE). (72) Inventors; and (75) Inventors/Applicants (for US only) : WILSON, Raymond, Lethbridge [GB/GB]; 3 Farmoss Road, Blundellsands, Liverpool L23 6UY (GB). DOKOUPIL, Jiri [DE/DE]; Hochstr. 9, D-6251 Gückingen (DE).		(74) Common Representative: DYNAVAC GMBH; Industriestr. 32, D-6252 Diez (DE). (81) Designated States: BR, JP, KR, SU, US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: LEATHER TREATMENT



(57) Abstract

In the techniques of colouring and otherwise fluid treating of skin or leather there exists the problem of effectively introducing a desired material, substance or agent deeply into the pores of the tissue of the skin or leather, and this without too much consumption of process time. The invention offers a solution to this problem by filling the pores of said skin or leather tissue with steam and then rapidly cooling down the steam-containing skin or leather by introduction into a bath fluid containing said material, substance or agent. Thereby the steam content is condensed and said fluid is sucked into the pores.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

Leather Treatment

This invention relates to treatment of leather and has particular application to colouring of leather.

5 The leather industry is one of the oldest known to man, and one of the most complex chemically, generally still relying on skills and techniques acquired and passed down through long practice, rather than wholly scientific analysis. Conventional
10 processes for colouring leather include soaking in liquid dyestuffs before during or after a stuffing or fat-liquoring process or processes required in finishing tanned leather to soft pliable form after the usual shaving splitting washing and bleaching
15 operations. Such colouration by soaking, whether or not accompanying stuffing or fat-liquoring, is usually done in rotating drums equipping with stirring paddles or agitators. Alternatives for achieving colouration include passing between rollers bearing dyestuff on
20 their surfaces, and passing through special dyestuffs having a solvent base and including penetration-promoting agents. Of these dyeing

processes, soaking in drums is probably the least convenient and presents control and reliability problems where dyestuff is part only of finishing agents in the drum; passing between dyestuff-coated rollers is probably the least effective in terms of penetration of dyestuff into the leather; and passing through dyestuffs with penetration-promoting agents is not popular, perhaps being least trusted as to its possible deleterious effects, the leather industry being highly conservative as is well-known to the present inventor from his life-long experience in that industry.

It is, however, believed that the leather industry should be ready for a clearly effective colouration process that is capable of operating on a continuous basis without introducing agents, such as the aforesaid penetration-promoting agents, whose use is not otherwise relevant to the skills and expertise involved in leather tanning.

According to one aspect of this invention, there is provided a process for treating animal skins in connection with making leather, which process serves to introduce into thickness of tissue of the skins a desired material substance or agent, and which process comprises introducing into the thickness of tissue of

the skins, typically into surface-communicating voids or pores of or established therein, a fluid having a high-volume state and a low-volume state at corresponding relatively high and low temperature, and
5 the process including occupation of said thickness of tissue of the skins by said fluid in its high-volume state then transition by cooling to get said low-volume state, in order to establish said desired material substance or agent in said thickness of tissue of the
10 skins.

In one embodiment of this invention, said fluid constitutes a medium by which said desired material substance or agent is infused or permeated directly into the leather before being effectively set therein
15 by said temperature lowering step. It is, of course, sufficient for such material substance or agent to be carried in dispersion by some medium having the required volume-reduction capability, i.e. not necessarily itself having that capability and then in
20 solid particulate or liquid droplet or other suitable form.

In other embodiments of this invention, said fluid serves only of itself to infuse or permeate into the leather and said desired material substance or
25 agent is presented to the leather afterwards, normally

in but feasibly before the temperature lowering step during which such material substance or agent is drawn into the leather by and as a result of volume reduction of said fluid infused or permeated into the leather.

5 Such presentation of said desired material substance or agent may be as a dispersion thereof in a space conveniently in a second fluid/medium occupying that space, into which the leather infused or permeated with the first fluid is passed and in which said temperature
10 reduction occurs. A liquid has been found to be satisfactory as the second fluid/medium, particularly where the desired material substance or agent is a dyestuff for colouration of leather.

It is further proposed that this invention be
15 applied beyond simple colouration of leather, and capable of achieving substantially through-penetration when applied to dry-crust. For example, it can be used to improve keying of materials substances or agents offering desired surface characteristics or features,
20 even to materials substances or agents required or desired in stuffing and fat-liquoring of leather to condition it and make it supple. Furthermore, the invention has been shown to produce some penetration even in the wet-blue state of skins or hides, and is
25 thus usable at that stage or in some state between

wet-blue and dry crust. Application to tanning substances as such is also envisaged, for example to obtain direct infusion or permeation of chrome salts, whether first in liquid solution or in particulate solid form, and there could be substantial savings of time and materials.

Reverting specifically to colouration, but not with the intention of limitation of teaching, a colouration process involves the steps of enhancing acceptance by leather of dyestuff by exposing the leather to a heated atmosphere or first fluid from which air is substantially excluded so that said atmosphere infuses or permeates the leather, and then passing the leather directly into contact with dyestuff at a lower temperature whereat said atmosphere substantially reduces its volume and is effective in drawing dyestuff into the leather. A suitable atmosphere or first fluid is a gas or vapour that liquifies or condenses at or above the temperature of the dyestuff, which may be or be contained in a liquid.

Such suitable infusing or permeating, volume-collapsing, atmosphere can, whether of its own nature or because of its temperature, can have beneficial effect by way of cleansing or purging leather tissue surfaces with which it comes into

contact, perhaps particularly by way of degreasing, even pore-cleaning or other void-forming action.

A satisfactory heated atmosphere giving highly satisfactory penetration of the leather is, as mentioned above, one where at least air in skin tissue is substantially displaced by steam, i.e. effectively an atmosphere consisting essentially of steam, and it is particularly effective to use steam that is dry, i.e. consisting substantially entirely of uncondensed water vapour and thus at a temperature actually above 100 degrees Centigrade. Using such steam temperatures, say up to about 120 degrees C, and exposure times of seconds, say 2 to 5 or 10 seconds, satisfactory penetration/purging occurs without any deleterious effects on tanned leather, indeed little actual increase in overall leather temperature in view of heat insulating properties thereof, but with permeation fully into the leather despite its rather dense nature as fibrous tissue. A closed system used for proving the present invention passes leather from steam directly into dyestuff, and it is not easy to measure actual leather surface temperature, nor penetration except for manifest resulting through-colouration, but the system seems not to be highly critical. No doubt there will be preferred or desirable variations

depending on the type and thickness of the leather.

Successful colouration in this way is considered to be a particularly surprising result for leather. Thus, chemically, steam is the same as water, and
5 manufacture of gelatin from imperfect animal skins unsuitable for making leather involves short pretreatment in lime and water at about 70 degrees Centigrade followed by extractions in hydrolising tanks at temperatures from 60 degrees Centigrade up to 100
10 degrees Centigrade. Higher temperatures for pretreatment are deleterious, even to gelatin production, and 100 degrees Centigrade is considered as a limit for the last extraction. Moreover, animal skins are, of course, effectively lost in the
15 production of gelatin. Accordingly, exposure and penetration of tanned leather to temperatures of 100 degrees Centigrade and above, even briefly during transit through a steam chamber, is something that the leather industry would expect to be deleterious rather
20 than beneficial.

It has, of course, been previously proposed that long textile webs can be finished on a continuous basis by a process involving steam purging prior to colouring or other finishing. However, textile materials are
25 essentially of an open filamentary nature, often with

substantial interstitial spaces even in its constituent yarn, and made up by weaving or knitting types, or of non-woven fibre-mat type, i.e. much more open than tanned leather. Moreover, textile materials are often specifically intended, indeed required, to withstand hot-water treatments, often including boiling, without sustaining damage. The present inventor is unaware of anyone in the leather industry, prior to this invention, giving any serious consideration to the use of temperatures at or above 100 degrees Centigrade, particularly using steam.

Development of this invention for colouration of tanned leather has been treated as first priority. However, given the satisfactory take-up of dyestuffs, and as mentioned above, it is only to be expected that take-up of other conditioning or finishing substances or agents will be similarly assisted, whether conventional substances or materials or agents or new or unusual substances materials or agents, and whether before or after tanning is complete.

In practice, exclusion of air between a steam chamber and a take-up bath is readily achieved by having the steam chamber exit extend below the surface of liquid contents of the take-up bath. Transport into and through the steam chamber can be by way of and on

one or more strand or mesh belts to promote free movement of steam throughout the steam chamber. An air excluding entry to the steam chamber can be by way of deformable rollers and/or brushes, aided, of course, by any inevitable over-pressure within the steam chamber compared with exterior ambient atmosphere.

Specific implementation of one embodiment of this invention will now be described, by way of example, with reference to the accompanying Fig.1 in which the single figure is a diagrammatic side view of continuous-feed steam-purging colouration apparatus 10 for tanned leather.

In the drawing a steam chamber 12 has steam porting indicated at 14 and 16 to an outer jacket or casing 20 and associated subsidiary distribution indicated at 24 and 26. As two steam portings and associated subsidiary distribution systems 14, 24 and 16, 26, one could operate for steam input and the other for steam output, or both may be used for input purposes as losses within the chamber should be low and a system of heaters within the outer jacket or casing 20 can serve to sustain a suitable dry-steam temperature, see coils indicated at 18, 22 (but feasibly at the exterior of a jacket or casing 20 of conductive nature). Heat loss through the jacket 20 is

shown minimised by using heavy insulation about the jacket or casing, see 30.

Steam entrant and distributed through the exterior casing or jacket 20 fills the whole chamber through inner discontinuous walling 32, 34 within which passes a conveyor system 36 between a chamber entry, shown as between the nip of two rollers 38A, 38B and a position above a chamber exit 40, see roller 40R. The chamber exit 40 is into a dyestuff bath 42 past a wall 40W that extends into the bath 42, actually below normal level 44L for liquid dyestuff 44.

Free movement and charging of steam throughout the chamber 12 is aided by use of a previous conveyor system 36, say of mesh or of multiple spaced strand type. A strand type is assumed for reasons that will become apparent.

The conveyor system 36 is further shown extending through the bath 42 on a downward slope into the dyestuff liquor, through two sets of guides 46, 48. which may be rows of rings or closed-off combs. The dye bath is shown with downwardly convergent forward and rearward sides generally following the downward and upward slopes of the strand conveyor, and then out of the dyestuff liquor on an upward slope, see bath exit roller 50.

A squeeze roller 52 is also indicated for aiding removal of excess dyestuff liquor and its return, conveniently down slope then into the bath 42 . The strand conveyor 36 is shown going over a roller 56 at a dyed skin discharge position 58, and there will be a return run to a skin loading position 60 before entry to the chamber 12.

It would, of course, be feasible to have the conveyor system 36 in separate segments, say one transversing just the dye bath 42 and squeeze station (or the dye bath only with a further conveyor through the squeeze station), and another transversing the steam chamber 12 and serving as input thereto (or entirely within the steam chamber 12 and receiving from a further conveyor and the rollers 38. The conveyor 36 could further be broken within the steam chamber, say to ensure that belt strands do not entirely prevent contact with steam, which could be done if consecutive strand conveyor portions have their strands in staggered relation.

A second conveyor system 60 is shown from the bottom of the dye bath and can effectively grip the skins at least lightly in order to aid upward feeding out of the dye bath. That conveyor system 60 could extend over the down sloped part of the conveyor 36 to

resist skins floating off in the bath, but then preferably spaced by more than the thickness of the skins to avoid marking their upper surface or shielding it from dyestuff. If a positive gripping feed
5 downwards is desired, another strand belt with its strands staggered relative to the upward running belt 60 could be used.

Exclusion of air at the steam chamber inlet is achievable if at least one of the rollers 38A, 38B is
10 readily deformable at contact with the entrant skin and/or with sealing brushes arranged beyond the rollers 38A,B which, at least then could be separable, see raising and lowering mount 70 spring-biassed down at 72, three-pivot roller-carrying plate 74 and
15 downward pressing ram/spring 76. An upward-movement-tolerant, downwardly-biasing system is also shown for the squeezer roller 52, see bias roller 80, medially pivotted carrier arm 82 and bias ram/spring 84.

20 The illustrated apparatus, including variants so far described, is intended only to be exemplary. For example, other than strand-belt conveyor systems could be used with suitable further variations, and the steam chamber could have vertically extending steam entry
25 and/or exit and distribution systems, indeed the skins

might be guided, even fall, vertically through a vertical steam chamber.

A further embodiment of the invention is shown in the accompanying Fig.2.

A leather piece 100 is shown to be advanced in a direction according to arrow 101 on a transport band 102. The path of the leather to be treated extends in horizontal direction firstly through the action range of a humidifying device 103, e.g. an arrangement of water spraying nozzles extending over the width of transport band 102. When leaving this station the leather will have a predetermined inherent humidity. It has to be understood that such humidifying station can be dismissed or left unused in case where the humidity of the leather in its input condition is sufficient for the further processing to be explained.

The leather then passes through a deviation device 104 comprising a lower deflecting roller 105 and an upper roller and holding band assembly 106, the latter being designed so as to secure the leather on its path along the upper surface of transport band 102 supported by said deflecting roller 105. The leather then moves along the descending section 106 of transport band 102 and through the rectangular cross-

section 107a of a microwave guide 107, which extends across the width of transport band 102 and thus of the leather piece, i.e. the waveguide extends rectangularly to the plane of Fig.1. Entrance and exit of the leather with respect to said waveguide cross-section is enabled by means of longitudinal slots 108 and 109 resp. extending along the lines bisecting the smaller sides of the rectangular waveguide cross-section and across the width of transport band 102. Waveguide 107 is connected via a double-curved section 107b to a microwave generator 110 of usual type.

As well-known in the art longitudinal slots arranged in a waveguide in the manner just explained allows for entrance and exit of planar articles to be treated in a microwave field without substantial escape of microwave energy, provided that an appropriate wave mode has been established and the width of said slots is not too great.

The lower waveguide slot 109 escapes immediately adjacent to or even slightly below the level of a colouring bath 111 into which transport band 102 and the leather are immerging after having passed the waveguide cross-section 107a. As any expert in the field is familiar with, the transport band has to be fabricated of a material substantially inabsorbent to microwave energy of the frequency in use. The microwave

energy is adjusted to a level sufficient for vaporising at least a substantial portion of the water bound in the leather according to its inherent humidity and thus to replace air (left in the leather according to its degree of humidity) by steam. When immersing into the colouring bath the steam now residing in the pores of the leather will be cooled down rapidly and brought to condensation, whereby the colouring liquid is sucked into the pores. An essential advantage of this embodiment is seen in avoiding a voluminous and expensive steam chamber.

CLAIMS

1. A process for treating animal skins in connection with making leather, which process serves to introduce into thickness of tissue of the skins a desired material substance or agent, and which process comprises introducing into the thickness of tissue of the skins a fluid having a high-volume state and a low-volume state at corresponding relatively high and low temperature, and the process including occupation of thickness of tissue of the skins by said fluid in its high-volume state then transition by cooling to get said low volume state in order to establish said desired material substance or agents in the thickness of tissue of the skins.
2. A process for treating animal skins in connection with making leather, which process serves to introduce into the skins a desired material substance or agent, and which process comprises introducing into surface-communicating voids or pores of or established in the skins a fluid having a high-volume state and a low-volume state at corresponding relatively high and low temperatures, and the process including occupation of said voids or pores by said fluid in its high-volume

state then transition by cooling to get said low volume state in order to establish said desired material substance or agent in said skins via said voids or pores.

5 3. A process according to claim 1 or claim 2, wherein said fluid constitutes a medium by which said desired material substance or agent is infused or permeated into the skin tissue before being left therein by said cooling step.

10 4. A process according to claim 1 or claim 2, wherein said desired material substance or agent is drawn into the skin tissue during the cooling step.

15 5. A process according to claim 4, wherein said desired material substance or agent is in a second fluid drawn into the skin tissue during the cooling step.

6. A process according to claim 5, wherein said second fluid is a liquid at a temperature effective to produce said cooling.

20 7. A process according to any preceding claim wherein said desired material substance or agent is effectively keyed to a surface of the leather.

8. A process according to any one of claims 1 to 6, wherein said desired material substance or agent
25 penetrates deeply into or through the skin tissue of

the leather.

9. A process according to claim 8, wherein the desired material substance or agent is a colourant.

10. A process according to any preceding claim,
5 wherein said fluid having high and low volume states is a gas of appropriate liquifying temperature.

11. A process according to any one of claims 1 to 10, wherein said fluid having high and low volume states is a vapour of appropriate condensing temperature.

10 12. A process for colouration of leather comprising the steps of exposing the leather to a steam atmosphere from which air and moisture are substantially excluded so that the steam infuses or permeates into the leather and then passing the leather directly into contact with
15 a medium carrying dyestuff and at a temperature at which the steam condenses and the dyestuff is drawn into the leather.

13. A process for treating animal skins in connection with making leather, which process serves to introduce into a skin having a certain water content a desired material, substance or agent, and which process comprises vaporising at least a substantial portion of said water content so as to establish a steam content filling at least part of the pores of the skin, and then introducing said steam containing skin into a fluid cooling bath containing said material, substance or agent so as to condense at least a substantial portion of said steam content such that the said material, substance or agent is sucked into the pores of the skin.

14. A process according to claim 13, wherein the skin before being exposed to said vaporising is humidified so as to establish a predetermined minimum water content.

15. An apparatus for carrying out the process according to claim 13 or 14, comprising a transport system for advancing at least one skin along a processing path which extends through at least one heating station (107, 107a) and at least one bath station including a bath container for liquid (111) containing a material, substance or agent to be introduced in said skin, said bath station being arranged subsequent to said heating station.

16. An apparatus according to claim 15, comprising at least one microwave heating station.

17. An apparatus according to claim 15 or 16, wherein said heating station comprises an outlet port for heated and steam-containing skin, said outlet port being arranged adjacent to or within the fluid of a subsequent bath station.

21

18. A process for treating animal skins in connection with making leather, which process serves to introduce into thickness of tissue of the skins a desired material, substance or agent, wherein the thickness of tissue of the skins contains a fluid having a high-volume state and a low-volume state at corresponding relatively high and low temperature, the process including occupation of thickness of tissue of the skins by said fluid in its high volume state then transition by cooling to get said low volume state in order to establish said desired material substance or agents in the thickness of the tissue of the skins.

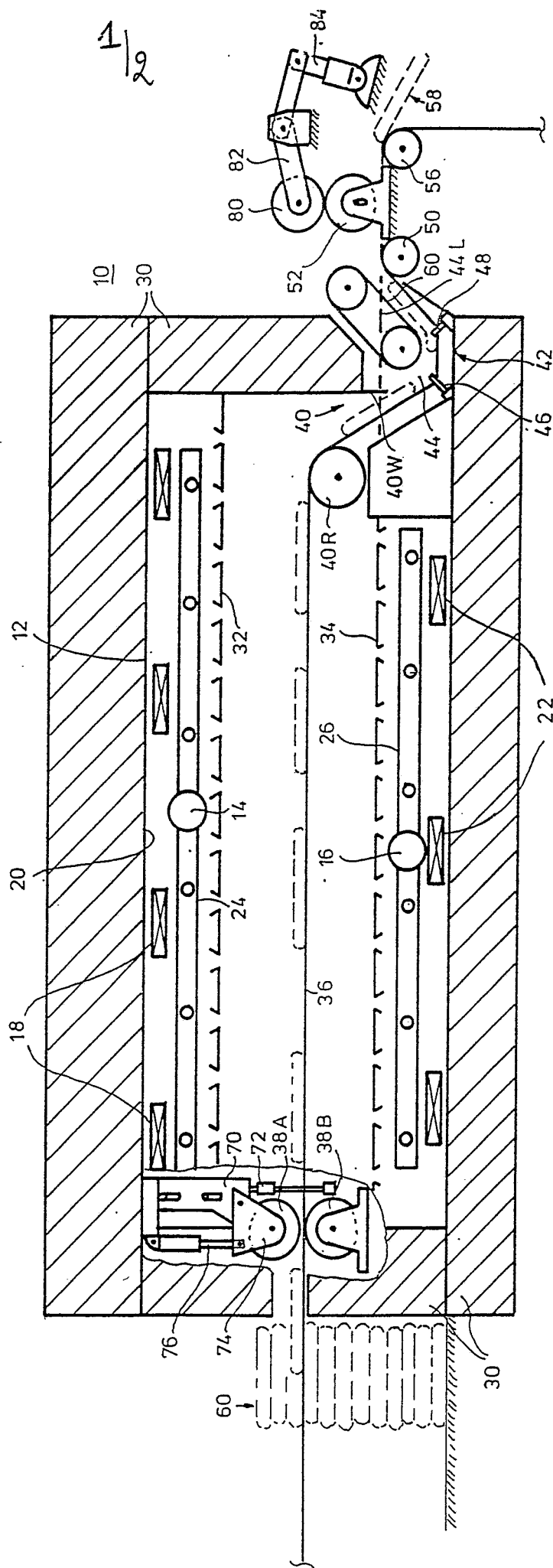


Fig. 1

2/2

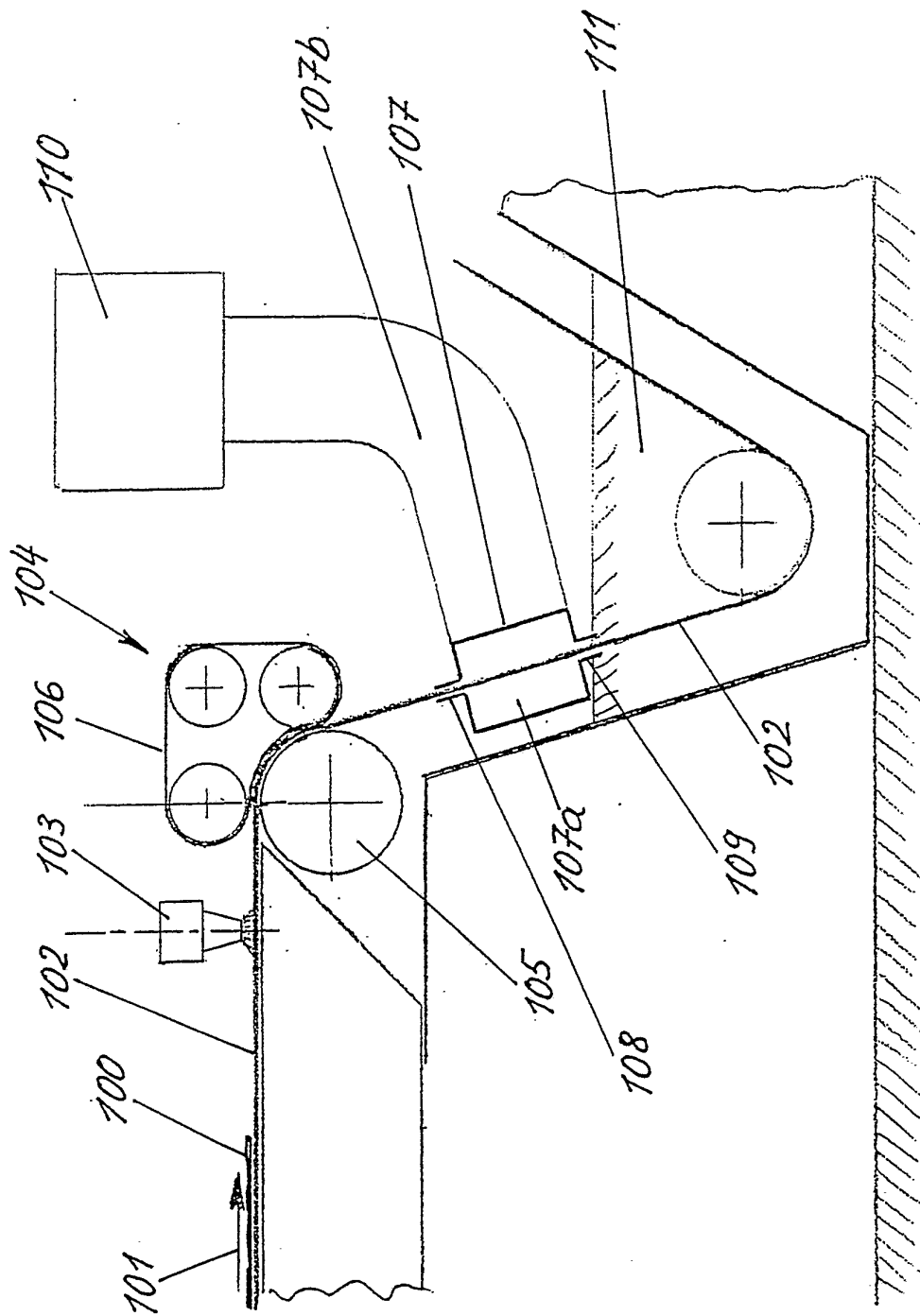
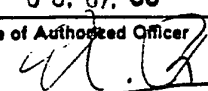


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/00088

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 14 C 15/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 14 C, D 06 B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	FR, A, 2452543 (VEB ROBUR-WERKE ZITTAU) 24 October 1980, see claims; figures 1,2 --	1
A	GB, A, 470777 (KODAK) 20 August 1937 ----	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
20th June 1989	06.07.89	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 L. BOSSI	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 8900088

SA 26831

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/06/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2452543	24-10-80	CH-A,B 631588	31-08-82
		DE-A,C 3003796	02-10-80
		GB-A,B 2045297	29-10-80
		NL-A- 8000090	01-10-80
<hr/>			
GB-A- 470777		None	
<hr/>			