Dec. 4, 1956 J. N. MASCI ET AL 2,773,000

HEMOSTATIC SURGICAL DRESSINGS

Filed June 6, 1952

Fig. 1.

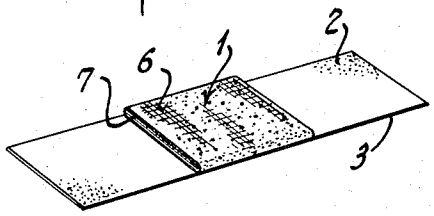


Fig. 2.

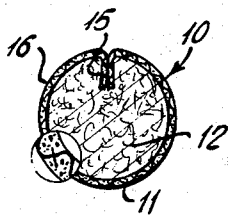


Fig. 3.

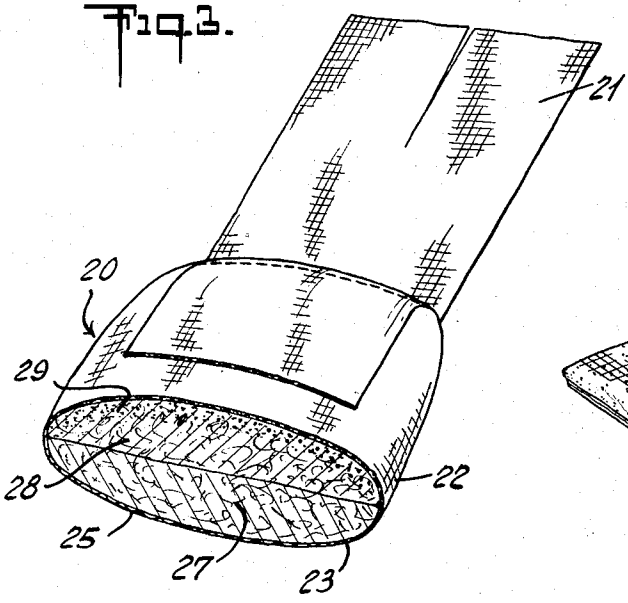
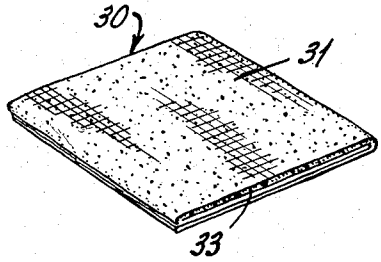


Fig. 4.



INVENTORS:
JOSEPH N. MASCI
WILLIAM H. ASHTON
JULIUS WILAND
BY
John C. Brumbaugh
ATTORNEY

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2,773,000

HEMOSTATIC SURGICAL DRESSINGS

Joseph N. Masci, Metuchen, N. J., William H. Ashton, Philadelphia, Pa., and Julius Wiland, New Brunswick, N. J., assignors to Johnson & Johnson, a corporation of New Jersey

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10 Claims. (Cl. 167—84)

This invention relates to hemostatic surgical dressings.

In checking the flow of blood from body wounds, it has been the well-known practice to apply to and hold with pressure against the affected areas suitable dressings which derive their effectiveness largely from the pressure employed. The principle of these conventional dressings has been to hold the blood within the general area of the wound until sufficient time has elapsed to permit the blood to coagulate and clot of its own accord. The blood, of course, permeates the dressing, be it gauze or other fibrous material, and when it clots acts as a bonding agent, securely uniting the dressing with the body. The fuzz which is normally associated with nonwoven and even woven dressings such as gauze augments this bond.

Other types of dressings have been developed with a view to minimizing the tendency of the ordinary dressing to absorb an undue amount of the blood. Various gums or other gel-forming materials have been added to the dressing in an effort to localize the blood by physical retention thereof within a confined space bounded by the relatively impermeable gum-treated dressing. No difference in principle has been introduced by the latter type of dressings, since the dressings themselves do not possess any inherent blood clotting properties, but merely attempt to retain the the blood within a relatively confined zone until the natural hemostatic qualities of the blood can come into play.

Each type of prior art dressing has often resulted in loss of an excessive amount of blood. Further, in many instances, it has been difficult, if not impossible, to keep the wound neat and sanitary for any length of time, and difficulties have arisen in removing the dressing caused by the tendency of the clot to adhere to the dressing and thereby start afresh the flow of blood.

An important object of the invention is to provide a surgical dressing which possesses inherent hemostatic, i. e., blood congealing, properties without the necessity of relying upon pressure and physical retention of the blood within the wound area for time sufficient to realize the normal tendency of the blood to clot itself.

A further object is to develop a hemostatic dressing which is readily removable from the wound, once hemostasis has been effected, with minimum disturbance of wound and congealed blood.

The surgical dressings of the present invention contain free acid cellulose glycolic acid ether (also called free acid carboxymethyl cellulose) or free acid cellulose hydroxypropionic acid ether (also known as free acid carboxyethyl cellulose) so disposed as to contact the wound when the dressing is placed in use; and further, a certain amount of non-toxic hydrophilic aliphatic poly-ol compound normally existing in non-crystalline condition. Each of the named cellulose derivatives (ethers) possesses remarkable and unexpected inherent blood congealing properties. The poly-ols permit the dressing to be removed from the wound without disturbing the clot and without altering the hemostatic activity of the cellulose

ether. Accordingly, the invention surgical dressings arrest bleeding much faster and possess properties described below which are substantially superior as compared with prior art dressings. Preferred dressings contain free acid cellulose glycolic acid ether hemostatic agent. In the specification terminology, the term cellulose glycolic acid ether (or carboxymethyl cellulose) includes both the free acid cellulose glycolic acid ether and its salts. Similarly, cellulose hydroxypropionic acid ether (or carboxyethyl cellulose) includes both the free acid cellulose hydroxypropionic acid ether and its salts.

The various embodiments of the invention may be conveniently understood by reference to the attached drawing, in which Fig. 1 represents a sectional perspective view of an invention BAND-AID Adhesive bandage. Fig. 2 describes a hemostatic globular surgical sponge, shown in section, of the type commonly used in tonsillectomies. Fig. 3 shows a sectional perspective view of a battle dressing prepared according to the invention. Fig. 4 is an illustration of a rectangular folded gauze dressing of the present invention.

Reference No. 1 indicates generally a folded gauze pad secured to adhesive face 2 of backing strip 3 of the adhesive bandage. Wound-contacting surface 6 of the dressing contains as an impregnant a hemostatic agent of the present invention, namely, free acid carboxymethyl cellulose or free acid carboxyethyl cellulose and a non-toxic hydrophilic aliphatic poly-ol compound normally existing in non-crystalline condition. The manner of incorporating this impregnant into the dressing will be described below. Zone 7 of pad 1 indicates the area of impregnated fibers. When the Fig. 1 adhesive bandage is placed on the body in wound-contacting position, exuding blood first contacts zone 7 and is quite promptly congealed, forming a block to further exudation of blood. Bleeding is therefore arrested with minimum loss and minimum penetration into the dressing. The bandage is preserved in substantially its original neat and cleanly condition. Further, when it is desired to remove the bandage, the small degree of penetration and the presence of the poly-ol minimizes tendency of the congealed blood to adhere to the dressing.

The surgical globular sponge shown generally at 10 comprises one or more layers of gauze 11 surrounding a core of gauze, cotton or other fibrous cellulosic material 12. The sponge may, if desired, be formed of all gauze or all cotton, suitably having the shell and core integral. The edges 15 of the gauze are tucked and tied or otherwise secured within the sponge. The gauze shell 11 is shown as containing in zone 16, as impregnant, a hemostatic agent plus a poly-ol compound of the present invention. In use, this hemostatic zone contacts the wound and arrests the flow of blood in a manner similar to that of the afore-described adhesive bandage.

Fig. 3 shows a battle dressing 20 in transverse section. The dressing is formed of body portion 22 and provided with tabs or ties 21. Body portion 22 is composed of shell 23 of gauze or other suitable material and core 25. The latter may suitably be in two sections, a first section 27 of non-absorbent cotton and a second section 28 of absorbent cotton. The ordinary function of section 28 would be to absorb and retain exuded blood and section 27 to prevent undue penetration of the blood into and through the dressing. According to the invention, the zone 29 comprising portion of gauze shell 23 and adjacent absorbent cotton contains as impregnant one of the hemostatic agents of the invention, i. e., free acid carboxymethyl cellulose or free acid carboxyethyl cellulose, plus the poly-ol compound.

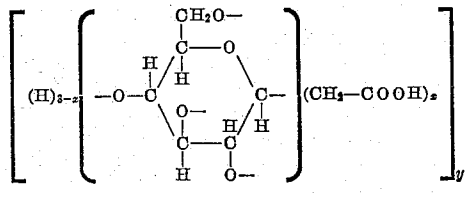
Dressing 30 of Fig. 4 is formed of a multiple of layers, which may be 8 to 16 or more in number, of folded gauze. The dressing has a wound-contacting surface 31

which is intended to be placed next to the body and held there by suitable bandage strapping or ties. Zone 33 adjacent surface 31 contains as impregnant in the fibers one of the invention hemostatic agents, plus poly-ol compound.

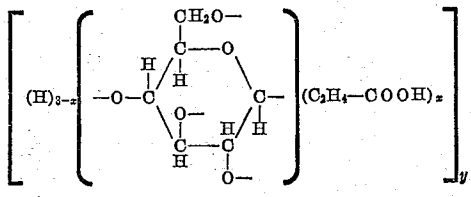
The poly-ol stripping agents, as indicated above are non-toxic, non-irritating, hydrophilic aliphatic compounds containing at least two hydroxyl groups or substituted hydroxyl groups which normally exist in non-crystalline condition, i. e., as a liquid, usually viscous liquid, or as a wax-like material. Suitable stripping agents include glycerin, propylene glycol, polyethylene glycols, and sorbitol. Esters of these alcohols are also included. For example, sorbitol may be utilized in the form of its ester, sorbitan monolaurate, and glycerin, or propylene glycol in the form of its various esters. Particular stripping agents are straight chain polyhydroxy compounds containing two to three hydroxyl groups per molecule or polymers (condensation products) thereof. Examples of this group are glycerin, glycols, and polyglycols. Glycerin is a preferred stripping agent. The stripping agent is used in amount sufficient to produce desired easy removal of the dressing. This amount, depending somewhat upon the amount of hemostatic agent present, will generally be at least about 1% by weight based on the dry weight of the dressing material in the impregnated zone. Excessive amounts of stripping agent may cause the dressing to have undesirable texture or appearance, and accordingly, the maximum percentage is about 25% on the same basis. A desirable range is about 3 to 12% stripping agent. It is preferred to maintain a ratio of stripping agent to hemostatic agent at least about 1.5/1.

The stripping agent may be incorporated into the dressing at any stage of its manufacture. For example, a conventient method is to dissolve it in the aqueous solution, described below, employed for adding hemostatic agent to the dressing material. If particular circumstances require, however, it may be added separately subsequent to the hemostatic agent, by applying an aqueous solution to the fabric and drying.

The carboxymethyl cellulose, also known as cellulose glycolic acid ether, which is used to prepare the surgical dressings of the invention may be described structurally as:

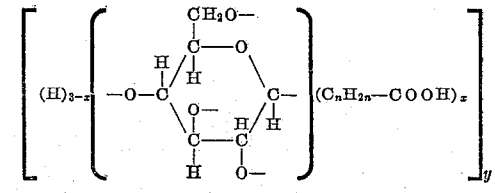


where x is not greater than 3 and y is a large whole number. The ring structure represents the anhydroglucose residue which is linked in known manner to similar residues on either sire to form a long chain cellulose structure. The bracketed H atoms are attached to oxygen atoms in the anhydroglucose residue in known fashion. Similarly, the (CH_2—COOH) groups are attached to the residue through oxygen linkage by substituting for the aforementioned H atoms. The carboxyethyl cellulose (cellulose hydroxy propionic acid ether), which is an alternate to the carboxymethyl cellulose, may be described structurally as:



x, again, being not greater than 3 and y a large whole number. The C_2H_4 group is preferably —CH_2—CH_2—.

The general formula of the materials used to prepare surgical dressings according to the invention is therefore:



where x is not greater than 3, n is 1 or 2, and y is a large whole number.

The degree of substitution (D. S.), a term commonly employed in connection with cellulose derivatives of the nature of the invention hemostatic agents, is an important property and indicates the average number of substituent groups per glucose unit in the cellulose molecular chain (i. e., the value of x in the above formulae). Since there are three hydroxyl groups and hence three possible points of substitution per glucose unit, the maximum D. S. is 3.0. It has been found according to the present invention that the degree of substitution is an important factor in determining the hemostatic activity of the particular cellulose ether. That is, as D. S. increases, hemostatic activity also increases. Hence, for the purpose of the present invention, material may be employed having D. S. which will afford adequate hemostatic activity. Preferably, since aqueous solutions (of the free acid or its salt) are conveniently used in adding the hemostatic material to the surgical dressing, material having D. S. which will afford water solubility of the salts (such as the ammonium or sodium salt) to produce suitable sizing solution is employed. Compounds having D. S. above about 0.5 generally have adequate hemostatic activity and further, are generally sufficiently soluble. Preferred cellulose ethers, have D. S. about 0.7 and above. The preferred maximum D. S. is about 2.0.

For invention purposes, consideration is given to the degree of polymerization (D. P.) of the cellulose derivatives (the value of y in the above formulae). At very low D. P.'s, water solubility may become quite high with corresponding deterioration in physical properties of the impregnant. Further, low molecular weight material is more difficult to convert to the preferred insoluble form by the heat treatment described below. Hence, D. P. expressed as viscosity reading in seconds on a modified Ostwald-Fenske viscosimeter pipette ASTM D-445 #300 of a 0.50% by weight aqueous solution of the free acid in a 0.50 N. NaOH solution at 25.50° C. should be at least about 5.7 seconds and may be as high as 36 seconds or greater, as compared with a zero pipette reading of 5.0 seconds for a 0.5 N. NaOH solution at the same temperature.

It is important to retain in the cellulose derivative impregnant an adequate number of carboxyl groups whose hydrogen atoms are not replaced by salt-forming radicals such as ammonium or alkali metal. In other words, the degree of neutralization (D. N.) should be maintained below certain limits. These free carboxyl groups apparently play a part in blood congealing in the hemostatic surgical dressings of the invention. Further, a certain number of free carboxyl groups is believed to be necessary to make the compound susceptible to conversion to preferred insoluble form as described below. D. N. is maintained not greater than about 60%, preferably 15% or lower. However, the sizing agent used to treat the surgical dressing to form the hemostatic dressing may be appreciably or completely neutralized as long as the D. N. is reduced in the final impregnant.

The hemostatic agents, whose structure and properties are described above, may be incorporated into the surgical dressing by a variety of procedures. Each of the procedures involves adding by one way or another free acid carboxymethyl cellulose or free acid carboxyethyl cellulose to the surgical dressing. The acid cellulose ether

may be so added, for example, by way of any of its soluble salts, soluble forms of the acid itself, or by synthesis of the cellulose ether in situ on cellulose fibers. A preferred procedure utilizes the ammonium salt of the cellulose derivative, which may be made by direct contact of free acid carboxymethyl or carboxyethyl cellulose powder with concentrated aqueous ammonium hydroxide solution. The latter solution is used at least in amount to supply NH_3 equivalent to the free COOH groups on the selected free acid cellulose derivative. The ammonium salt is then diluted with water to any desired concentration and used directly as a treating agent added to the surgical dressing, the solution preferably also containing poly-ol stripping agent. If desired, the free acid carboxymethyl cellulose used for preparation of the ammonium salt may be synthesized by acidification of the sodium salt, using mineral acid if the acid cellulose derivative has degree of substitution in the insoluble range, and mineral acid plus alcohol if the acid cellulose derivative is soluble in water, and filtration of the acid cellulose derivative.

Free acid carboxymethyl cellulose was prepared, for example, by steeping 20 parts (by weight) of sodium carboxymethyl cellulose in 500 parts of a mixture of 1,000 parts isopropanol to 200 parts concentrated hydrochloric acid for two hours. The liquid was then removed and steeping repeated with an equal and fresh amount of isopropanol-HCl. The solid material was then washed with a mixture of 80 parts isopropanol and 20 parts water until free of mineral acid and sodium chloride. The converted free acid carboxymethyl cellulose powder was then filtered and dried in air at room temperature. The dried powder was treated with ammonium hydroxide solution containing NH_3 in amount equivalent to the carboxyl groups in the acid carboxymethyl cellulose. The resulting solution of ammonium carboxymethyl cellulose was then diluted with water to 2% by weight strength.

The ammonium salt is incorporated into the surgical dressing in amounts indicated below. After treating and drying, the dressing material is heated at temperature to bring about decomposition of the ammonium salt into NH_3 and the free acid cellulose derivative. The latter is preferably further converted into a form which has been found to be quite insoluble in water and may be properly described as "refractory." The formation of the refractory hemostatic agent is brought about by carefully controlling the temperature at and the time during which the treated material is heated. In general, elevated temperatures are necessary to bring about the change. Formation of refractory acid impregnant begins to take place at an appreciable rate at about 175° F. At this temperature, it takes at least about 30 minutes to effect a substantial decrease in solubility of the acid as compared with the acid-treated and dried but non-heat treated material. Conversion takes place at a substantially faster rate at temperatures of at least about 200° F. Heating time in each case is preferably at least about 30 minutes. Within the heating time of about 2½ to 3 hours, optimum insolubility is obtained.

Temperatures above about 235° F. generally afford substantially higher rates of conversion of the soluble to the insoluble forms of hemostatic agent. Preferably, for fast operation and correspondingly short heating times, temperatures are maintained above about 300° F. The temperature in any case is maintained below levels at which excessive degradation of the cellulose ether treating agent, base fabric of the surgical dressing or stripping agent occurs within the minimum time in which the material can be handled at the elevated temperatures in question. Preferably it is held below about 350° F.

Any source of heat is suitable for insolubilizing the hemostatic agent. Hot air or infra-red ovens, induction heating devices, steam, hot plates, or heated irons may be used. In large scale operation, hot air ovens, which are standard equipment in many factories, are preferred.

Although the ammonium salt affords a convenient way of incorporating the free acid cellulose derivative into the surgical dressing, the invention is not limited to the use of the ammonium salt. An alternative procedure is to treat the surgical dressing material with the sodium salt, for example, in an aqueous solution, and thereafter form the free acid cellulose derivative in situ on the fibers by addition of a stronger acid, such as hydrochloric acid or a mixture of such acid and precipitating alcohol. The acidified material is washed thoroughly with water to remove excess reagents, the stripping agent added, and dried. The treatment described is preferably then followed by heating to form the refractory free acid carboxymethyl cellulose just as in the case of the ammonium salt.

As a further alternative procedure, a water solution of the free acid cellulose derivative may be prepared (if cellulose ether which is water soluble in the acid form is used) by adding an excess of HCl to a 2% solution of the sodium salt. This can be dialyzed using a semi-permeable membrane, to remove the excess mineral acid and NaCl and leave free acid cellulose ether in solution. This free acid carboxymethyl cellulose solution, to which stripping agent may be added, is then used to treat the surgical dressing material. The material is then dried and preferably heated at the elevated temperatures indicated above to obtain invention surgical dressing having insoluble hemostatic agent impregnant.

Another method for incorporating the invention hemostatic agents into cellulosic surgical dressing materials, such as cotton or gauze, comprises first treating the cellulose derivative with caustic soda or potash to form the alkali metal derivative, then reacting this derivative with an alkali metal salt of chloroacetic acid. The conditions of the reaction can be controlled to maintain the physical state of the reacted fibers of cellulosic material which can be washed free of reagents and converted to the free acid carboxymethyl cellulose by treatment with a solution of a mineral acid. Washing, drying, and preferably heat treatment to form the refractory cellulose derivative follow.

It will now be apparent that it is not necessary to impregnate the surgical dressing after it is fabricated. In fact, in most instances it will be found convenient to add the impregnant to the surgical dressing material before fabrication of the dressing. For example, in the case of the adhesive bandage of Fig. 1, zone **7** of the dressing pad **1**, containing hemostatic agent and stripping agent, may be a separate layer of gauze superjacent to other gauze which does not contain impregnant. Similarly, the gauze shell **11** of globular sponge **10** may be impregnated and treated as above prior to fabrication of the sponge.

The invention surgical dressings are advantageously constructed of woven fibrous material or nonwoven fibrous material having a suitable bonding agent. However, unbonded nonwoven fibrous dressings also may be advantageously formed according to the invention. Hemostatic properties and easy removal of the invention surgical dressings may be found and surgical dressings formed, for example, of non-fibrous material which have sufficient absorbency, permeability, and other desired properties. Non-cellulosic dressings may be substituted for the usual cotton as a base material for the dressing.

In bandages having gauze as the base carrier material for hemostatic agent, the thread count of the gauze should be sufficiently high so that porosity is not excessive. On the other hand, the thread count should not be unduly high so as to produce harshness. In view of these considerations, it is preferred to utilize gauze having thread count in the range from about 14 x 10 to about 64 x 56. This range gives satisfactory dressings covering a suitable range of physical properties, texture, and efficacy. Within these limits there is a special preferance for gauze of 20 x 12 or 28 x 24. The gauze count has some bearing on preferred amount of hemostatic agent incorporated into the dressing.

As indicated, the zone containing hemostatic agent is disposed adjacent the wound-contacting external surface. The precise location and depth of this zone is subject to

considerable variation. It is, however, preferably disposed at or as nearly as possible adjacent to the outside surface of the dressing. For appreciable blood clotting effect, the hemostatic zone should contain at least about 0.3 mg. of hemostatic cellulose derivative per square inch of wound-contacting surface. A preferred amount is at least about 0.8 mg. per square inch. Larger amounts may be used, and the zone of hemostatic agent may be extended as far into and through the dressing as desired. For the purpose of retaining flexibility of the dressing, however, it is preferred to maintain the concentration of hemostatic agent in the zone of fibers containing the same not greater than 10% by weight based on dry impregnated fibers. The optimum range of coating weight is influenced to some extent by thread count of the gauze. There is special preference for 3 to 3½% of free acid on dry weight basis using 20 x 12 gauze. As the thread count is increased, the upper limit of practicable coating weight decreases. Thus, a coating weight of 3 to 4% on 44 x 36 gauze may still be satisfactory but somewhat harsh, whereas on the 14 x 10 gauze it would be considerably softer.

The various procedures illustrated above for incorporating carboxymethyl cellulose or carboxyethyl cellulose into surgical dressing material each involve forming an aqueous solution of the cellulose derivative in one chemical form or another and treating the surgical dressing material with this aqueous solution. Other procedures may be used, however, if desired. For example, the carboxymethyl or carboxyethyl cellulose in suitable form may be dissolved in organic solvents in cases where it is soluble therein, and formed solutions used to treat the material, followed by drying and preferably heat treating.

Following are examples of the invention, in which parts and percentages are expressed on a weight basis.

Example 1

Cellulose glycolic acid ether ammonium salt having degree of substitution of 1.2 and degree of polymerization indicated by viscosity of 0.50% by weight aqueous solution of the free acid in 0.50 N. NaOH at 25.50° C. equal to 26.8 seconds as determined on a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for 0.50 N. NaOH solution at the same temperature, was made into aqueous solution of 2.7% concentration. The solution was made up from the dry free acid carboxymethyl cellulose powder by adding an excess of aqueous ammonium hydroxide thereto. After dilution with water to adjust the concentration to 2.7%, the solution was heated in a steam jacketed kettle at about 200° F. to remove excess NH_3. Heating was continued until pH was 7.0. The solution was then used to impregnate 44 x 36 gauze full width (40 inches). The gauze, after treatment, was passed between mangle rolls so adjusted as to produce 150% pickup of solution by the gauze. The wet gauze was passed through a tenter oven maintained at temperatures between 275° F. and 300° F. The residence time of the gauze in the oven was about 12 minutes, which was sufficient to convert the ammonium salt to the free acid carboxymethyl cellulose, and the latter further to the insoluble "refractory" form. The dry solids pickup by the gauze was 4%.

The gauze treated as above was then passed through a bath consisting of 4.7% aqueous glycerin solution and re-run through a tenter dryer at the same temperature, but at a velocity corresponding to a 6-minute bake. The dried material contained 7% glycerin on a dry basis corresponding with 150% pickup of glycerin solution. The treated gauze was sampled and tested for hemostatic activity in the liver and spleen of the adult albino rat. Incisions were made and portions of gauze (4 plies, 1 cm. square) placed on the wounds without pressure. The gauze covered the wounds. The time was noted in minutes and seconds for the blood to cease flowing.

	Liver	*Spleen*
Treated gauze	50″	1'25″
	55″	1'20″

After hemostasis had been effected, the gauze was removed from the wounds. The gauze did not adhere to the clot nor break the clot when it was removed.

Example 2

The procedure of Example 1 was repeated with the exception that the gauze containing heat treated (refractory) acid carboxymethyl cellulose impregnant was treated to incorporate, instead of glycerin, a polyethylene glycol wax, named by the manufacturer "Carbowax 1500." The treated gauze contained 20% of this wax based on the dry gauze. This gauze was tested for hemostasis in the same way as was the gauze described in Example 1. The results were substantially the same as the results of Example 1 from the standpoint of hemostasis and removability of the gauze from the clot.

Example 3

A sample of 44 x 36 gauze was treated with a 2% aqueous solution of carboxymethyl cellulose sodium salt having degree of substitution of 1.2 and degree of polymerization corresponding to free acid voscosity of 26.8 seconds determined by the method outlined in Example 1. The pickup of solution was about 500%. The gauze was dried in air under room conditions and the coating converted to the free acid carboxymethyl cellulose by steeping in a mixture of 80 parts ethyl alcohol and 20 parts concentrated aqueous hydrochloric acid for about 20 minutes. It was then washed in running water until free of mineral acid and inorganic salts and again dried in air at room temperature. At this point the coating assayed 9.2% on a dry basis. The coated gauze was divided into 2 parts and 1 part given treatment of glycerin in the following way. The material was soaked for one minute in a solution of 80 parts water and 20 parts glycerin and passed between wringer rolls to obtain pickup of between 100% and 120%. The glycerin content was about 22% on a dry coated gauze basis. The three types of samples were then evaluated for hemostasis and adhesion in rat organs according to the procedure of Example 1. Incisions of similar type and size were made for each test. Examples were #1, plain gauze; #2, coated gauze; #3, coated gauze, glycerin treated. Four plies of gauze 1 cm. .square were used for each test pad. The results were as follows:

RAT LIVER

Sample	Bleeding Time	Adhesion to Clot
#1	7'7″	adheres.
#1	7'15″	Do.
#1	7'20″	Do.
#2	48″	Do.
#2	1'0″	Do.
#3	40″	does not adhere.
#3	40″	Do.

RAT SPLEEN

Sample	Bleeding Time	Adhesion to Clot
#1	19'56″	adheres.
#1	19'6″	Do.
#2	1'45″	Do.
#2	2'3″	Do.
#3	1'20″	does not adhere.
#3	1'16″	Do.

RAT KIDNEY

Sample	Bleeding Time	Adhesion to Clot
#1	22'20"	adheres.
#1	19'46"	Do.
#2	1'35"	Do.
#2	1'54"	Do.
#3	50"	does not adhere.
#3	1'30"	Do.

Example 4

A sample of one-inch wide gauze having thread count approximately 50 x 40 was treated with a 3% aqueous solution of sodium carboxymethyl cellulose having degree of substitution of 1.2 and degree of polymerization corresponding with free acid viscosity of 26.8 seconds. Excess solution was squeezed out between wringer rolls at a pressure sufficient to leave 7% dry solids impregnated in the gauze. The coated gauze was then dried in air at room temperature. The superficial coating of cellulose derivative was converted to free acid ether by soaking the gauze in a mixture of 1000 parts 95% ethanol, 200 parts concentrated aqueous hydrochloric acid, and 125 parts water. It was then washed four times in water to remove all free mineral acids and salts and dried. The impregnated gauze was soaked for two minutes in an aqueous 20% glycerin solution and passed between wringer rolls to produce material having 100% solution pickup. The treated gauze was autoclaved at 240° F. for 30 minutes and evaluated for hemostasis on the rat. Control tests were carried out on plain (untreated) gauze. The test pads contained 4 plies of gauze in each case. Results were as follows:

BLEEDING TIME

Site	Plain Gauze Control	Treated Gauze
Muscle	5'20"	1'30", 1'35"
Liver	7'7"	59", 1'10"
Kidney	19'46"	1'21", 1'22"
Spleen	19'6"	2'10", 2'9"

The treated gauze in each case was removable from the wound without disturbing the wound or clot, whereas the plain gauze could not be so removed without disturbing the clot.

Example 5

A sample of 44 x 36 cotton gauze is treated with 5% by weight aqueous solution of sodium salt of carboxymethyl cellulose having degree of substitution of 0.90 and degree of polymerization corresponding to free acid viscosity of 8.4 seconds. The treated gauze, containing about 8 mg. of sodium carboxymethyl cellulose per square inch, is dried on a stretcher. It is then treated with aqueous alcoholic hydrochloric acid to convert the sodium salt to the free cellulose derivative acid, washed free of excess inorganic acid and salt, and dried. The treated gauze is impregnated with aqueous solution of 5% glycerin and squeezed out to produce 200% solution pickup, and dried. The treated gauze, upon being tested for hemostatic activity in the rat, is found to be substantially more hemostatic than untreated gauze, and substantially more easily removed from the wound after hemostasis without disturbing the clot than is hemostatic gauze containing no glycerin or similar poly-ol compound.

Example 6

Sterile surgical absorbent cotton is saturated with a 2% aqueous solution of carboxymethyl cellulose sodium salt with degree of substitution of 1.17 and degree of polymerization corresponding with free acid viscosity of 18.3 seconds as measured by the Example 1 procedure, and dried in air. The dried material may contain about 5% of the sodium salt. The material is then washed for two hours in a mixture of 80 parts ethanol and 20 parts aqueous hydrochloric acid, and the sodium salt thereby converted to acid carboxymethyl cellulose. It is rinsed free of mineral acid and salt, in water and dried. The treated cotton is impregnated with a "stripping agent" solution of 5% glycerin in water or 10% "Carbowax 1500" in water to 200% solution pickup, and dried. In each case the cotton treated with stripping agent is found to be more easily removed from clots than is similar gauze untreated with stripping agent, and to stop flow of blood much more quickly than does similar cotton not treated with free acid cellulose ether hemostatic agent.

The foregoing description is presented as illustrative and it will be apparent that there are many modifications within the spirit and scope of the invention. Hence, the invention is to be limited only by the appended claims.

We claim:

1. A surgical dressing having adjacent a wound-contacting external surface thereof, a non-toxic hydrophilic aliphatic poly-ol compound normally existing in non-crystalline condition and in amount sufficient to produce easy removal of said dressing from a clot of blood, said dressing also containing cellulose derivative of the group consisting of free acid cellulose glycolic acid ether and free acid cellulose hydroxypropionic acid ether in hemostatic amount at least about 0.30 mg. per square inch of said surface, said cellulose derivative having degree of substitution at least about 0.5 and degree of neutralization in the approximate range of 0 to 60% and sufficiently low so that the free carboxy content of the cellulose is at least 0.5 per glucose unit, said cellulose derivative further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature.

2. A surgical dressing having in amount sufficient to produce easy removal of said dressing from a clot of blood, a polyhydroxy compound of the group consisting of straight chain compounds having 2 to 3 hydroxyl groups per molecule and condensation products thereof normally existing in non-crystalline condition, said dressing also containing free acid cellulose glycolic acid ether adjacent a wound-contacting external surface thereof in amount at least about 0.30 mg. per square inch of said surface, said free acid cellulose ether having degree of substitution at least about 0.5 and degree of neutralization in the approximate range 0 to 60% and sufficiently low so that the free carboxy content of the cellulose is at least 0.5 per glucose unit, said free acid cellulose ether further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N. NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature.

3. A sterile fibrous surgical dressing containing as an impregnant adjacent a wound-contacting external surface thereof, and in amount sufficient to produce easy removal of said dressing from a clot of blood, a polyhydroxy compound of the group consisting of straight chain compounds having 2 to 3 hydroxyl groups per molecule and condensation products thereof normally existing in non-crystalline condition, said dressing also containing adjacent said surface free acid cellulose glycolic acid ether in amount at least about 0.30 mg. per square inch of said surface, said free acid cellulose ether having degree of substitution at least about 0.5 and degree of neutralization in the approximate range 0 to 60% and sufficiently low so that the free carboxy content of the cellulose is at least 0.5 per glucose unit, said free acid cellulose ether

further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N. NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature.

4. A sterile fibrous surgical dressing containing as an impregnant adjacent a wound-contacting external surface thereof, at least about 1% based on impregnated fibers of a polyhydroxy compound of the group consisting of straight chain compounds having 2 to 3 hydroxyl groups per molecule and condensation products thereof normally existing in non-crystalline condition, said dressing also containing adjacent said surface free acid cellulose glycolic acid ether in amount at least about 0.30 mg. per square inch of said surface, said free acid cellulose ether having degree of substtitution at least about 0.7 and degree of neutralization in the approximate range 0 to 15% and sufficiently low so that the free carboxy content of the cellulose is at least 0.7 per glucose unit, said free acid cellulose ether further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N. NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature.

5. A sterile fibrous surgical dressing containing as an impregnant adjacent a wound-contacting external surface thereof, 3 to 12% glycerin based on impregnated fibers, said dressing also containing adjacent said surface free acid cellulose glycolic acid ether in amount at least about 0.8 mg. per square inch of said surface but not greater than about 5% by weight based on impregnated fibers, said free acid cellulose ether having degree of substitution at least about 0.7 and degree of neutralization in the approximate range 0 to 15% and sufficiently low so that the free carboxy content of the cellulose is at least 0.7 per glucose unit, said free acid cellulose ether further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N. NaOH solution at 25.50° C. of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature.

6. A sterile fibrous surgical dressing containing as an impregnant adjacent a wound-contacting external surface thereof, 3 to 12% glycerin based on impregnated fibers, said dressing also containing adjacent said surface, free acid cellulose glycolic acid ether in amount at least about 0.8 mg. per square inch of said surface but not greater than about 5% by weight based on impregnated fibers, said free acid cellulose ether having degree of substitution at least about 0.7 and degree of neutralization in the approximate range 0 to 15% and sufficiently low so that the free carboxy content of the cellulose is at least 0.7 per glucose unit, said free acid cellulose ether further having degree of polymerization indicated by viscosity of a 0.50% by weight solution of the free acid in a 0.50 N. NaOH solution at 25.50° C of at least 5.7 seconds as determined in a modified Ostwald-Fenske viscosimeter pipette ASTM D–445 #300, as compared with a zero pipette reading of 5.0 seconds for a 0.50 N. NaOH solution at the same temperature, and having been heated, after treatment of the dressing therewith, at a temperaure above about 175° F. for time sufficient to form free acid cellulose ether having substantially lower water solubility.

7. A hemostatic surgical dressing having an external surface adapted to contact the wound and containing a non-toxic hydrophilic aliphatic poly-ol compound normally existing in non-crystalline condition on said surface in amount to produce easy removal of said dressing from a clot of blood, said dressing also containing cellulose derivative of the group consisting of free acid cellulose glycolic acid ether and free acid cellulose hydroxypropionic acid ether having degree of substitution at least about 0.5 and degree of neutralization in the approximate range of 0 to 60%, but sufficiently low so that the free carboxy content of the cellulose is at least 0.5 per glucose unit, adjacent said wound-contacting external surface in amount at least about 0.30 mg. per square inch of said surface.

8. A sterile fibrous surgical dressing according to claim 7.

9. A surgical dressing according to claim 7 in which the cellulose derivative is free acid cellulose glycolic acid ether.

10. A surgical dressing according to claim 7 in which the cellulose derivative has been heated after treatment of the dressing therewith at a temperature above about 175° F. for time sufficient to form cellulose derivative having substantially lower water solubility.

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