United States Patent Office 2,805,913 Patented Sept. 10, 1957

2,805,913

METHOD OF ENHANCING FILLING POWER, STABILIZING CURL, ETC., IN LAND FOWL FEATHERS BY APPLYING GLYOXAL AND PRODUCTS PRODUCED THEREFROM

Edward R. Frederick and Michael C. Jaskowski, Pittsburgh, Pa., assignors to the United States of America as represented by the Secretary of the Army

No Drawing. Application February 19, 1954, Serial No. 411,594

16 Claims. (Cl. 8—94.10)

This invention relates to a method of treating land fowl feathers, especially chicken feathers, to increase their "filling power" and resiliency, and to impart permanent curliness and water repellency, thereby making such feathers an acceptable substitute for the standard waterfowl down and feather mixture now in wide use for sleeping bags, etc. Another object is to lower the cost of treating such feathers. A further object is to make handling of chicken feathers easier, not only with respect to the elimination of malodorous products normally found on chicken feathers but also easier and less expensive handling in the factory, as will be explained. A further object is to employ a single chemical which will kill bacteria, insects and other organisms on the feathers, and will eliminate bad odors and also will react with any blood left on the feathers. An additional object is to facilitate drying the treated feathers by employing a chemical which apparently prevents hydrolyzing of the keratin of the feathers. A still further object is to provide a surface finish to the treated feathers. Another object is to provide an effective method of producing feather fibers, free of quills and shafts, without resorting to cutting, milling and similar mechanical steps. Other objects will be apparent from the following description of the method presently preferred by us.

In explanation of the expression "filling power," reference may be made to the report entitled "A Proposed Method for Measuring the Filling Power of Down and Feathers," by Henry A. Sinski, publication No. TD103037, The Office of Technical Services, Department of Commerce, and to the article by N. B. Edelman in Textile Research Journal, vol. 17, p. 199 (April 1947) entitled "Investigation of methods for determining the filling power of feathers." See also the Sinski et al. Patent No. 2,706,910 dated April 26, 1955.

The term "feathers" as used herein includes clean and soiled land fowl feathers, crushed (commercial "curled") land fowl feathers, land fowl feather fibers, stripped land fowl feathers, and mixtures of these, but not waterfowl feathers or down.

This application is a continuation-in-part of our abandoned application Ser. No. 359,948 filed June 5, 1953, entitled "Glyoxal Process for Modifying Chicken Feathers and the Like."

In the preferred procedure of the present invention, the feathers, if not known to be entirely free of blood, are soaked for about ten minutes at about 110°–125° F. in a solution of 1 oz. "Haemo-Sol" to 10 gallons of water. "Haemo-Sol" is a commercial haemolytic agent or blood solubilizer in wide use by hospitals and laboratories for dissolving blood and cleansing instruments and laboratory equipment, manufactured by Polychem Corporation, 501 Fifth Ave., New York 17, N. Y. Another commercial blood solubilizer which might be used as sold under the name "Coagusol." After soaking, the solution is drained from the feathers and the feathers are then laundered or dry cleaned. In laundering, preferably a detergent such as Tergitol NPX is used (0.25% water solution at 110°–125° F.). Other detergents which have been found to be satisfactory are sold under the trade marks or names "Sted," "Glim," "Triton," "Sterox" and "Monsanto MXP." In general, the nonionic type of detergents should be used to avoid any action on the protein of the feathers. Laundering continues for about twenty minutes, then the solution is separated from the feathers by centrifuging or wringing. At this point it should be explained that a number of well known dry cleaning solutions could be used to clean the feathers, but washing or laundering is preferred because it is less expensive. Both laundering and dry cleaning may take place in the same vessel or container that is used during the soaking (blood-solubilizing) step. Of course if the feathers as initially received are perfectly clean, the soaking and washing or dry cleaning may be omitted.

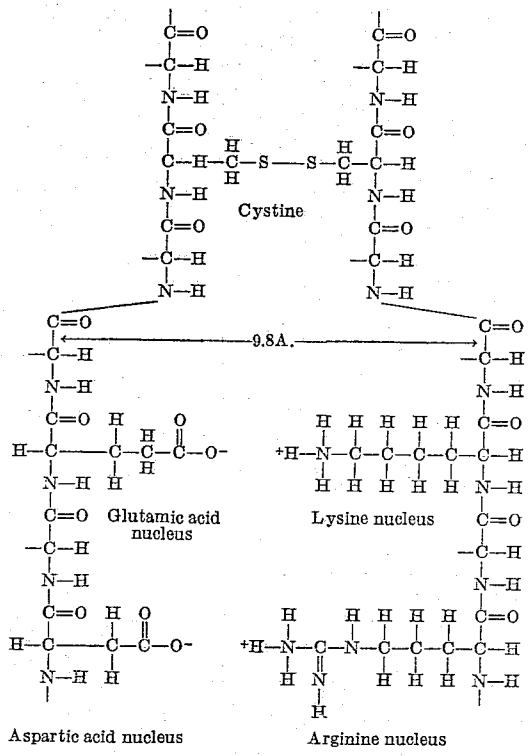
If the feathers are from immature chickens, the damp feathers from the described laundering or dry cleaning operation are placed in a 1% water solution of trisodium phosphate $Na_3PO_4.12H_2O$ at 110°–120° F. for about ten minutes. If feathers from mature chickens are being processed, the phosphate treatment period is increased to about thirty minutes. This mild alkaline treatment of the feathers is believed to alter the stability of the feathers by modification of cystine linkages in the keratin. (One cystine link is shown in the structural representation of keratin written below.) This is an important but not essential step in the glyoxal processing of feathers and its purpose is to materially increase the curliness of the feathers, and to curl naturally uncurly mature feathers, thereby to increase the bulk value of the final feather product. Other suitably buffered alkaline solutions may be used in lieu of the trisodium phosphate solution mentioned above; but in all cases the time of the treatment must be much less for immature feathers to avoid excessive degradation. It is believed that the higher concentration of cystine linkages in mature feathers enables them to resist the action of the alkaline solution for a longer period.

The drained and rinsed product from the curling step just described is immersed in a solution of preferably 1% glyoxal plus 0.05% chromium fluoride ($CrF_3.4H_2O$) at 110°–120° F. By "1% glyoxal" we mean 1% by weight of pure glyoxal OHCCHO (diformyl or oxalaldehyde). In lieu of chromium fluoride, which is a catalytic agent, about 0.1% of technical aluminum sulphate $Al_2(SO_4)_3$ may be used, or a somewhat larger amount of magnesium silicofluoride $MgSiF_6$. The pH should be between 2 and 4, which insures a good penetration of the feather body. We prefer chromium fluoride because it not only is an effective catalyst: it serves to prevent bacterial degradation of feathers. Aluminum sulphate does have the ability to lower the pH of the commercial glyoxal solution and probably the aluminum reacts with the carboxyl groups which are made available for reaction by the glyoxal-amine tie-up, as will be apparent later on. Both "pure"

and "commercial" glyoxal (30%) have been mentioned in the foregoing. Commercial glyoxal will be used if pure glyoxal is too expensive or is unavailable, and if used, its proportion will be increased to equal 1% (by weight) pure glyoxal solution. The desired acidity (pH 2–4) is attained by merely adding one of the named catalysts to the glyoxal. The reaction may also be carried out with a neutral or slightly alkaline solution (pH=7.6 to 8.0), which causes the reaction to proceed farther (to judge from appearances) on the feather surface, but does not seem to penetrate to the interior of the feather structure, hence is less effective. In view of these observed facts, we claim a pH range of 2–8 in the glyoxal treatment of feathers.

The principal reaction of glyoxal on the feather keratin is believed to be along the lines indicated in the following representations of a keratin molecule before, during and after the treatment.

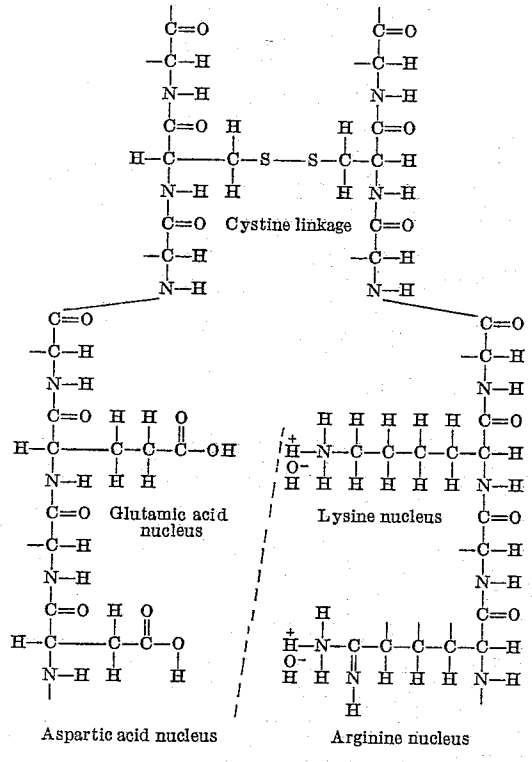
FEATHER KERATIN MOLECULE (PART) BEFORE TREATMENT



In the above picture of a keratin molecule, a cystine bond and two inner salt linkages are shown, forming what might be termed a three-rung ladder. When all the rungs are intact, the structure is quite resistant to deformation. Opening the inner salt linkages, which is easily accomplished below or above the isoelectric point, would allow the main backbone structure to orient, twist, shrink or elongate. Thus if it is assumed that an improved feather form involves the transition of alpha keratin to beta keratin, the mere opening of the cystine linkages would permit subsequent reversion to the contracted normal alpha keratin. So long as the inner salt linkages are free to open, the structure cannot be fixed and such conditions as mere wetting are adequate to bring about the transition. By examining the spacing and character of the inner salt linkages, it is found that the inner salt bond is sufficiently large to accommodate the water molecule. It is known from X-ray studies that the wetting of keratin, increasing this spacing from 9.8 A. to 10.8 A., is conclusive evidence of the plasticizing effect of water on keratin. The sensitivity of feather keratin to water, noted by softening and swelling, is apparently

a direct result of the affinity of water for the polar groups in the linkages and the ability of the space between the salt linkages to accommodate the water molecule.

PLASTICIZED (HYDROLYZED) FEATHER KERATIN MOLECULE (PART)

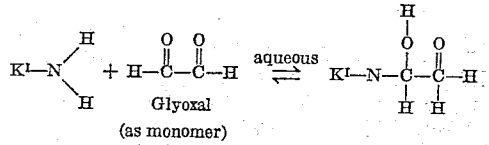


The reduction of the distance between the backbone chains and the inclusion of non-polar groups in the inner salt linkages theoretically should reduce the sensitivity of feather keratin to moisture. This result we believe we accomplished by the glyoxal reaction.

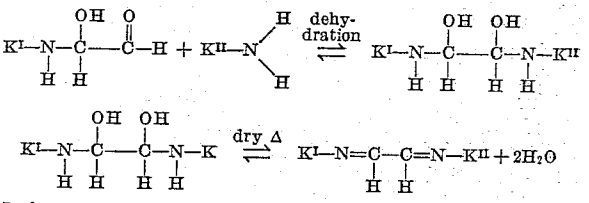
GLYOXAL-ALUMINUM SULPHATE TREATMENT OF CHICKEN FEATHERS

(*Possible reactions at low concentrations and moderate temperatures simplified*)

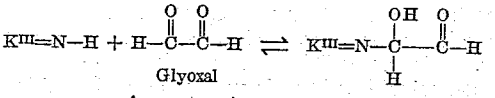
Amine groups:

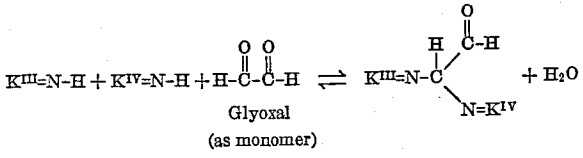


i. e. lysine group

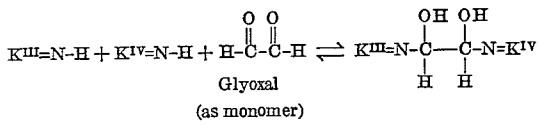


Imine groups:

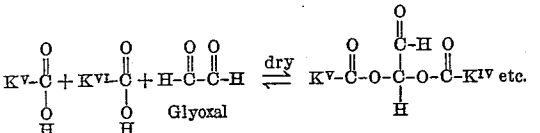


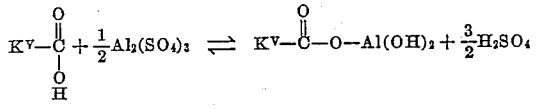


or

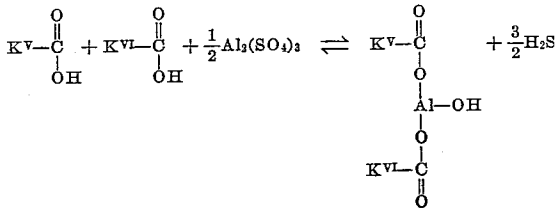


Carboxyl groups:

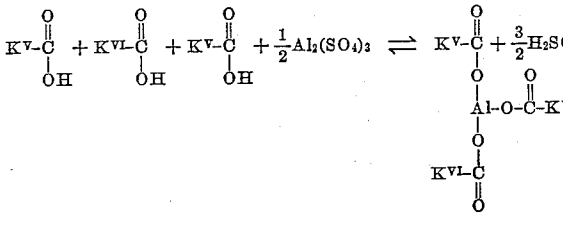




or



or



NOTES:

(1) The extent of reaction between reagent and groups in keratin containing active hydrogen is dependent upon proximity of these groups.

(2) K^{I}, K^{II}, etc.,=keratin molecule other than active group indicated.

Glyoxal reacts on feathers to modify and fix the keratin structure, thus stabilizing the curl produced by nature or by previous processing.

After the glyoxal treatment but before curing, the feathers are rinsed and partly dried by centrifugal wringing, etc. The rinsing following the glyoxal treatment is important to remove any impurities such as glycols left from the glyoxal. However, this rinsing need not proceed at once: the damp feathers may be left in open containers for days without further attention. No odor attends them, except a faint and pleasant odor from the glyoxal. This is a very important operating advantage as a factory following our process could shut down for a holiday or a weekend without the necessity of going on with the process. With some other feather processes, the feathers would be ruined unless work continued after soaking.

The 1% glyoxal solution mentioned above causes a very slight yellowing of white feathers, the color being almost entirely concentrated on the shafts and quills. The treated, dried feathers are very soft, are permanently curly and water repellent, have a faint, pleasant odor,

and are ready for use as a filling material without further treatment. Their filling power is in the range of 6.0 to 6.4.

Instead of a 1% solution, a 5% or even a 10% solution of glyoxal, with the same amount of catalytic agent, may be employed. A 10% glyoxal solution produces a much brighter and more uniform yellow coloring of white feathers, including the barbs and barbules as well as the shafts and quills. The temperature of the glyoxal solution should not exceed 125° F. for best results. Treatment at 140°–145° F. will make a large proportion of fine fibers and feather fragments, while at 180° F. about 100% of the feathers will be reduced to feather fibers. It should be particularly noted that the only change necessary in the process to produce feather fibers is to raise the temperature.

In connection with the curl of land fowl feathers, it should be explained that curl seems to be affected by the maturity of the fowl, as well as by the breed: young fowl feathers have more curl than the feathers from mature birds, and white feathers, generally speaking, have a more pronounced curl than pigmented feathers. The curling step is very important to insure a curl, but if the feathers are so graded that all of them are naturally curly, the curling step can be omitted.

The described process is simple and relatively inexpensive. Commercial glyoxal comes on the market in steel drums and with 30% purity costs about 19¢ a pound. Glyoxal is known to be a rust inhibitor, hence operating difficulties arising from corrosion of metal equipment are unlikely to arise from its use.

Formaldehyde, which has been in use for some time when working with feathers, is a choking, suffocating, highly reactive gas that is difficult to work with, whereas glyoxal has a pleasant odor and is easy to work with. Furthermore, formaldehyde, though useful in tanning hides and in the treatment of wool keratin, is not satisfactory in the treatment of feather keratin, and has little effect even at a pH of 8, where it is known to react best. Glyoxal not only kills bacteria, organisms, insects and odors: it also reacts with the coagulated blood often adhering to feathers to produce a powdery product which is not *per se* offensive but must be removed if the feathers are to meet Army specifications. It is less expensive to remove the blood on feathers by soaking them in a blood solubilizing solution, as described above, than to react glyoxal with blood to produce a powder and then remove the powder from the dried feathers. Hence blood removal before the glyoxal treatment is important (though not absolutely essential). Blood clots on feathers will act as barriers to resins applied later on to enhance the filling power of the feathers. Another distinct advantage of our process is that the treated feathers dry more rapidly and more completely. Apparently the reason for this is that water is not absorbed by the glyoxal-treated feathers, hence is squeezed or wrung out more readily, being almost entirely on the feather surfaces.

It has been observed that glyoxal first reduces the water sensitivity of chicken feathers and finally (after curing) imparts outstanding water resistance with form fixation. Until several hours have passed after drying the feathers, they display only a moderate degree of water resistance, but if the feathers are allowed to age, or if they are cured at 200–240° F. for thirty minutes, they acquire a remarkable water resistance. Curled and glyoxal treated feathers will maintain their curl in the presence of 100% relative humidity (i. e., immersed in a bath of water) for at least three weeks. Furthermore, if these treated curled feathers are restrained in a straight form under high (100%) humidity for a long period, their curl will return when the restraining medium is removed.

Feathers treated in accordance with our invention are in perfect condition for a subsequent wax, resin, or wax plus hydrophobic silica gel treatment, as disclosed in the patents of E. R. Frederick Nos. 2,715,086 and 2,714,561 dated respectively August 9, 1955 and August 2, 1955,

The rinsed product of the preceding step may be immersed in a solution containing 1.5% wax-phenolic mixture, which is added substantively to such a degree that practically all will be taken up by the feathers. Products of our invention may also be treated with a resin-forming composition which is then treated to condense in situ to form the resin on the feathers. Following any of these steps, the feathers will be rinsed and then picked and fluffed by means of apparatus such as that disclosed in the Frederick, Jaskowski and Haller Patent No. 2,739,391 dated March 27, 1956. After drying and fluffing the feathers, curing may take place either in the same machine or on a conveyor passing through an oven, for example, with the fluffed feathers exposed to a temperature of about 200°–250° F. for at least five minutes or as much as half an hour.

The following table compiled from laboratory notebooks at the Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania, shows the effect of our process on the filling power of straight chicken feathers (not fractionated).

Table

Run Symbol	Feather Treatment	Filling Power (cm.)	
		Conditioned	Wet Wall
P-76	Laundered at 140°–145° F. and brush-picked.	2.2	1.6
P-15c	Laundered and extracted with CCl_4 and brushed-picked.	3.4	3.3
P-23	Laundered and extracted with CCl_4. Wax plus hydrophobic silica gel added. Brush-picked. Dried in fluffing machine at 145° F.	6+	6.0
P-16a-1	Laundered. 1% Glyoxal plus $Al_2(SO_4)_3$. Brush-picked and oven-cured at 248° F. for one-half hour.	5.8	5.7
P-55b-1	do	6.4	6.4
P-58c	do	5.9	6.0
P-72a	Laundered. 1% Glyoxal plus $Al_2(SO_4)_3$. Brush-picked and oven-cured at 248° F. for 1 hr.	6.0	6.0
P-33b	Laundered. 1% Glyoxal plus $Al_2(SO_4)_3$. Brush-picked and dried in fluffing machine at 145° F.	4.9	4.8
P-33c-2	The product of Run P-33b treated with wax plus hydrophobic silica gel. Brush-picked and oven cured at 248° F. for one-half hour.	(1)	(1)
P-85c	Laundered. 1% Glyoxal plus $Al_2(SO_4)_3$, with pH 7.6 and temp. 110° F. followed by fluffer cure at 200°–240° F.	5.6	5.7

[1] Much greater than 6.

The considerable variation in filling power values, observed in hundreds of tests, is unquestionably due in part to the inherent characteristics of the feathers, and in part to the treatment of the feathers during and following plucking. Feathers which have been subjected to gross neglect after plucking may have their filling power lowered as much as 50% or more. The breed of the chicken is also important. Feathers from Indian River (white) fowl consistently yield products of greater bulk properties (after treatment) than feathers similarly processed from Rhode Island Red, Barred Rock or Leghorn chickens.

The products of our invention would be an excellent substitute for kapok (an imported product), hence could be used for filling cushions, comforters and sleeping bags. Indeed, wherever goose and duck feathers or goose and duck down are now used, chicken feathers treated as described above may be used, with considerable savings as will be appreciated.

What we claim is:

1. A method of treating land fowl feathers to impart many desirable characteristics, one of which is an enhanced filling power brought about by stabilizing the curl present naturally in the feathers or produced by previous processing, which comprises soaking the curled land fowl feathers in a water solution of 1% to 10% glyoxal plus a catalytic amount of a catalytic agent, the pH of the bath being between 2 and 8, the temperature of the bath ranging between 90° F. and 180° F., and the time of treatment being sufficient to fix the curl in the land fowl feathers; then rinsing and drying the feathers.

2. The method defined in claim 1, wherein the bath has a strength of 1% by weight of pure glyoxal, the pH is 2–4, the temperature is 90°–125° F., and the time of the treatment is about half an hour.

3. The method defined in claim 1, wherein the catalytic agent is 0.1 aluminum sulphate and the pH between 2 and 4.

4. The method defined in claim 1, wherein the catalytic agent is 1% magnesium silicofluoride and the pH is between 2 and 4.

5. The method defined in claim 1, wherein the catalytic agent is 0.05% chromium fluoride and the pH is between 2 and 4.

6. The method defined in claim 1, wherein the land fowl feathers are treated in a 10% glyoxal-water solution plus a catalytic amount of a catalytic agent, the temperature being about 180° F. and the pH being about 7.6 to 8, the time of the treatment being sufficiently long to reduce substantially all the feathers to feather fibers.

7. The method defined in claim 1, wherein the land fowl feathers as first received lack the desired degree of curliness and are soaked in a curl-inducing alkaline bath for a sufficient length of time to substantially curl the feathers, then are removed from the bath and rinsed before the glyoxal treatment.

8. The method defined in claim 7, wherein the catalytic agent is 0.1% aluminum sulphate and the pH is between 2 and 4.

9. The method defined in claim 7, wherein the catalytic agent is 1% magnesium silicofluoride and the pH is between 2 and 4.

10. The method defined in claim 7, wherein the catalytic agent is 0.05% chromium fluoride and the pH is between 2 and 4.

11. The method defined in claim 7, wherein the curl-inducing solution is a 1% water solution of trisodium phosphate at 110°–120° F., the time of the treatment being 10 to 30 minutes according to the maturity of the land fowl feathers.

12. Land fowl feathers whose curl has been fixed by the process defined in claim 1.

13. Land fowl feathers whose curl has been fixed by the process defined in claim 2.

14. The final product produced by the method defined in claim 6.

15. Land fowl feathers whose curl has been induced and fixed by the process defined in claim 7.

16. Land fowl feathers whose curl has been induced and fixed by the process defined in claim 11.

References Cited in the file of this patent

UNITED STATES PATENTS

2,129,219	Koga	Sept. 6, 1938
2,390,073	Calva	Dec. 4, 1945
2,441,859	Weisberg et al.	May 18, 1948
2,521,328	Beer	Sept. 5, 1950
2,524,042	Croston et al.	Oct. 3, 1950
2,530,175	Pfeffer et al.	Nov. 14, 1950
2,547,060	Tillisch	Apr. 3, 1951

FOREIGN PATENTS

611,331	Great Britain	Oct. 28, 1948

OTHER REFERENCES

Am. Dyestuff Rep., Sept. 8, 1947, pp. 515, 516.