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ACROLEIN TREATMENT OF FEATHERS

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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 down and feather mixture now in wide use for sleeping bags, comforters, etc. A further object is to treat feathers so as to make them resistant to moths and microbiological attack. Other objects will be apparent from the following description of the method presently preferred by me.

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. TD-103037, 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. Ordinarily, chicken feathers have a filling power of 1.8 to 2.1 cm., while the 40/60 down-feather mixture has a filling power of 5.3 to 5.9 cm.

The term "feathers" as used herein includes whole land fowl feathers of the desired size range, crushed (commercial "curled") land fowl feathers, land fowl feather fibers, stripped land fowl feathers, and mixtures of these.

In the preferred procedure, the feathers, if not known to be entirely free from blood, are first soaked for about ten minutes at about 110°–125° F. in a water solution of a commercial blood solubilizer, such as Coagusol (a mixture of sodium hexametaphosphate and alcohol sulfate). After the 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" (alkyl phenyl ether of polyethylene glycol) is used (0.25% water solution at 110°–125° F.). Other non-ionic detergents have been found to be satisfactory. In general, the non-ionic type of detergents should be used to obviate any action on the protein of the feathers. Laundering continues for about twenty minutes, then the solution is removed from the feathers by centrifuging or wringing. While a number of well-known dry cleaning solutions could be used to clean the feathers, 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 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 43°–49° C. 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 the cystine linkages in the keratin. This step is important because it materially increases the curliness of the feathers and it curls naturally uncurly mature feathers, thereby to increase the bulk value of the final feather product. Other suitably buffered alkaline solutions, for example, sodium carbonate or borax, may be used in lieu of the phosphate solution mentioned above, but in all cases the time of the treatment must be less for immature feathers to avoid excessive degradation. Trisodium phosphate is preferred because of its quicker action due to a higher pH. 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.

I now proceed to describe a number of feather treatments with aqueous acrolein solutions in accordance with my invention, at temperatures of about 35°–46° C., based on laboratory runs at The Tanners' Council Research Laboratory, University of Cincinnati.

ACROLEIN TREATMENT WITH SUNLIGHT

A 45 gram batch of chicken feathers was soaked in a sodium phosphate solution, as above described, for thirty minutes at 42°–43° C. Then the feathers were well-rinsed with water and were placed in a 2% bath of acrolein (acrylaldehyde), an unsaturated aldehyde. This bath was composed of 23.5 ml. of acrolein, 1 gram of aluminum sulfate, 1000 ml. of water and enough dilute acid to give a pH of 2–3. In lieu of aluminum sulfate, chromium acetate or ferrous ammonium sulfate may be used. The feathers remained in the bath for 45 minutes at a temperature of 38°–45° C. The feathers in the bath were then exposed to sunlight for fifteen minutes at 44° C., thus making the aggregate time of immersion of the feathers in the acrolein bath about one hour up to this point. Then the pH was raised to 7 by adding dilute Na_2CO_3, the bath still being exposed to sunlight for fifteen more minutes. The vessel containing the feathers was then placed in a warm water bath in a hood and kept there for fifteen additional minutes, the total reaction time being ninety minutes. Then the feathers were thoroughly rinsed, dried and cured at 87°–89° C. The filling power immediately after the cure was 6.2, but after aging for nine months, the filling power was found to be 6.6 to 7.0. After laundering the treated feathers, drying in bags and relaxing, the filling power was 6.5, a better figure than that noted at the conclusion of the run. The feathers showed definite resistance to papain digestion, which is a good indication that they will resist microbiological attack.

HYDRAZINE—ACROLEIN TREATMENT

A batch of 45 grams of chicken feathers, after the described phosphate soak and rinse, was treated with a 0.1% hydrazine solution, pH 8, at 33°–35° C. for fifteen minutes; then the feathers were removed from the solution and well rinsed with water. Next the feathers were immersed in an acrolein solution of a strength slightly above 2% (26 ml. acrolein in 1000 ml. of water) at about 5.5 pH for thirty minutes at 43°–46° C. No metallic ions were present as in the treatment described above. Then acid was added to lower the pH to 2 and the bath was maintained at 43° C. for thirty minutes. Next, in order to allow the double bond to react, the pH of the solution was raised to 7.5–8.0 and kept for twenty minutes at 40°

C. The pH was further raised to 10–11 and the bath was warmed to 43°–46° C., this portion of the treatment continuing for thirty minutes. Then the feathers were thoroughly rinsed, dried and cured at 87° C. The filling power of these feathers was 6.2. After laundering, drying and letting them relax, the feathers still had a filling power of 6.2. Moreover, the feathers were definitely enzyme-resistant.

ACROLEIN POLYMERIZATION IN SITU

A batch of 67 grams of chicken feathers was given the phosphate soak described above, then was well rinsed in water. Next the damp feathers were immersed for fifteen minutes in a ferrous ammonium sulfate solution made up from 12 grams $Fe(NH_4)_2(SO_4)_2.6H_2O$ in 1500 ml. of water. Then the feathers without rinsing were transferred to a 6% acrolein solution containing 10 ml. of 30% hydrogen peroxide. It should be noted here that the transfer without rinsing is essential and the strength of the solution is important. The ferrous ion in the presence of hydrogen peroxide is oxidized to the ferric ion, which produces a hydroxyl ion and a free radical HO· or OH^+ which initiates a polymerization. Benzoyl peroxide (benzoyl superoxide) or other initiator could have been used in lieu of H_2O_2. The feathers were kept in the acrolein bath for 180 minutes at pH 4.5 and 35°–46° C., during which period they turned an apricot color. Then they were rinsed, dried and cured. Filling power, 6.2. After the treated feathers had been laundered, dried in channels (to simulate conditions in a sleeping bag) and allowed to relax, their filling power was 6.1.

The following table gives data relative to experimental acrolein treatments:

Table I

SHOWING EFFECT OF TREATMENT OF CHICKEN FEATHERS WITH ACROLEIN UNDER DIFFERENT pH

Run No.	Lot No.	Pretreatment	Reaction pH	Filling Power in cm.
37	6	trisodium phosphate.	2.0–7.0	5.6
38	6	do	2.0–7.0	5.8
53	7	do	2.0–7.0	6.2
84	9	do	9.0–9.5	5.6
85	9	do	2.0–7.0	5.8
86	9	do	7.5–9.5 3.0–4.0	5.6
87	9	do	3.5–5.0 9.5–10.0 2.0–3.0	5.5

The feathers from run No. 38 of the above table were laundered and after drying and relaxing showed an increased filling power, viz., 5.9.

Table II

SHOWING EFFECT OF ACROLEIN TREATMENT ON HIGH GRADE CHICKEN FEATHERS FROM IMMATURE CHICKENS (FILLING POWER 3.7 CM.)

Run No.	Pretreatment		Time in Minutes	Initial to Final pH Levels	Filling Power in cm.
	Reagent	pH			
100	0.1% hydrazine	8	15	5.5–2.0–7.5–8.0–10.0–11.0.	5.7
101	trisodium phosphate.	11+	40	5.5–2.0–7.5–8.0–10.0–11.0.	6.2
	0.1% hydrazine	8	15		
102	trisodium phosphate.	11+	40	5.5–10.0–2.0	5.7
	0.1% hydrazine	8	15		
103	trisodium phosphate.	11+	40	5.5–7.5–8.0–10.0–2.0.	5.7
	0.1% hydrazine	8	15		
104	trisodium phosphate.	11+	40	no acrolein treatment.	5.5
	0.1% hydrazine	8	15		

Table III

SHOWING EFFECT OF ACROLEIN TREATMENT ON DRUM WASHED FEATHERS FROM IMMATURE WHITE ROCK CHICKENS (FILLING POWER 4.3 CM.)

Run No.	Metallic Salt	Acrolein, Sol. Percent	Reaction pH	Filling Power
230	Chromium Acetate 2 g.	2	9.0–2.8–6.6	5.7
231	First treated with aluminum sulphate, then with acrolein.	2	9.6–2.8–6.6	6.5
232	Chromium Acetate 2 g.	2	9.3–2.9–6.9	5.8
233	Aluminum sulphate 2 g.	2	2.8–6.8	5.9
234	First treated with hydrazine sol. then 2 g. chromium acetate.	2	9.6–2.8–6.6	6.1
235	Ferrous ammonium sulphate plus H_2O_2.	6	4.5	6.2
237	do	6	4.4	6.3
240	do	[1] 8	4.5	6.1

[1] Cloudy, partially polymerized before use.

The only aldehyde-treated feathers which are known to show complete resistance to papain-bisulphite digestion are acrolein-treated feathers, regardless of the presence of metallic ions in the acrolein treatment. This suggests that some kind of a cross-linking has taken place. Polymerization experiments were quite successful when a 6% acrolein solution was used in the presence of hydrogen peroxide after the feathers had been dipped into a 0.02 mole ferrous ammonium sulphate solution. No apparent polymerization took place when only 2% acrolein or 8% cloudy, partially polymerized acrolein was used. In acrolein-treated feathers, whenever a filling power of 6.1–6.5 was obtained, the number of loose barbs was reduced. Acrolein-treated feathers seem to improve on aging. Feathers from eleven-weeks old Arbor Acres chickens treated with a 2% acrolein solution in the presence of 1 gram of aluminum sulphate at pH 2–3 and then at 7.0, showed a filling power of 6.2 Nine months later, under adverse conditions with a relative humidity of 75–80% and a defective (warped) piston of the Sinski filling power apparatus, the filling power of the same lot of feathers was 6.6. Thus, it is clear that acrolein, probably because it is unsaturated, gives better results than almost any other aldehyde. In this connection, reference should be made to the copending application of Varsenig Z. Pasternak and Robert M. Lollar, Serial No. 658,900, filed concurrently herewith, now Patent No. 2,886,399, dated May 12, 1959, entitled "Aldehyde Treatment of Land Fowl Feathers."

Having described my invention, I claim:

1. A method of treating land fowl feathers to enhance their filling power, which comprises modifying the cystine linkage of the keratin of said land fowl feathers by soaking said feathers in an aqueous alkaline solution, rinsing said feathers, then placing the feathers in an about 2%–6% aqueous solution of acrolein having an initial pH of about 2–5.5 and at a temperature of about 35°–46° C., said solution containing a catalytic amount of a member of the group consisting of aluminum sulfate, chromium acetate and ferrous ammonium sulfate, then increasing the pH of the solution to about 7–11, keeping said feathers in said solution until their filling power is increased, then rinsing and drying the feathers.

2. The method according to claim 1, wherein said aqueous alkaline solution is an approximately 1% solution of trisodium phosphate.

3. The method according to claim 1, wherein said aqueous alkaline solution is a mildly alkaline hydrazine solution.

4. The method according to claim 1, wherein said feathers are soaked, prior to said acrolein treatment, first in an aqueous trisodium phosphate solution having a pH of about 11, rinsed, then soaked in a mildly alkaline dilute aqueous hydrazine solution, and rinsed.

5. A method of treating land fowl feathers to enhance their filling power, which comprises modifying the cystine

linkage of the keratin of said land fowl feathers by soaking said feathers in an aqueous alkaline solution, rinsing said feathers, then placing said land fowl feathers for about one hour in an aqueous acrolein bath having a temperature above room temperature and containing a catalytic amount of a member of the group consisting of aluminum sulfate, chromium acetate and ferrous ammonium sulfate, the pH of said bath being about 2–3, then raising the pH of the bath to about 7 by adding a mildly alkaline solution, exposing the bath and the feathers therein to sunlight having a catalytic action for about half an hour, partly before and partly after neutralizing the solution, and allowing the reaction to continue above room temperature until the filling power of the feathers is increased, in the absence of such light, then rinsing and drying said feathers.

6. A method of treating land fowl feathers to enhance their filling power, which comprises treating the land fowl feathers with an about 0.1% hydrazine solution of about pH 8, at about 33°–35° C. for about fifteen minutes; removing the feathers and rinsing them; then immersing the feathers in an aqueous solution of acrolein of a strength slightly above 2% at pH about 5.5 for about thirty minutes at about 43°–46° C.; then lowering the pH to about 2 with the bath maintained at about 43° C. for about 30 minutes; then raising the pH to about 7.5–8.0 and holding the temperature at about 40° C. for about 20 minutes; then raising the pH to about 10–11 and holding the temperature at about 43°–46° C. for about 30 minutes; then rinsing the feathers and drying them.

7. A method of treating land fowl feathers with acrolein to enhance their filling power, which comprises modifying the cystine linkage of the keratin of said land fowl feathers by soaking said feathers in an aqueous alkaline solution, rinsing said feathers; then immersing the feathers, prior to the acrolein treatment, for about

15 minutes in a ferrous ammonium sulfate solution, the ferrous ammonium sulfate contents of said solution being of sufficient strength to exert a catalytic effect during the subsequent acrolein treatment; then without rinsing the feathers transferring them to an about 6% aqueous acrolein solution containing a catalytic amount of an oxidizing peroxide catalyst, whereby said acrolein is at least partly polymerized in situ, and keeping the feathers in the bath for about 180 minutes at a pH of about 4.5 and a temperature of about 35°–46° C.; then rinsing the feathers and drying them.

8. A method of treating land fowl feathers with acrolein to enhance their filling power, which comprises immersing the land fowl feathers, prior to the acrolein treatment, for about 15 minutes in a ferrous ammonium sulfate solution, the ferrous ammonium sulfate contents of said solution being of sufficient strength to exert a catalytic effect during the subsequent acrolein treatment; then without rinsing the feathers transferring them to an about 6% aqueous acrolein solution containing a catalytic amount of an oxidizing peroxide catalyst, whereby said acrolein is at least partly polymerized in situ, and keeping the feathers in the bath for about 180 minutes at a pH of about 4.5 and a temperature of about 35°–46° C.; then rinsing the feathers and drying them.

9. The product produced by the method of claim 1.

10. The product produced by the method of claim 6.

11. The product produced by the method of claim 8.

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