GLUE
and
GELATINE

By

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PREFACE

THE greatest importance is now attached to the glue and gelatine industry which, dependent as it is on the by-products of the hide and skin and allied trades, supplies so many industries with materials necessary for the production of a wide range of products from munition waddings and casings to pharmaceuticals. Natural protein glues are, in spite of the advances made by synthetic cements, still of the greatest value as adhesives and the demand for them far exceeds the supply. During 1941 there was a considerable shortage of hide glue materials, resulting in some price increases as high as several hundred per cent. Price control of hide glue stock and hide glue has since been announced by the U. S. Office of Price Administration and in Great Britain the war emergency has entailed Government stabilization of both raw material and finished glues.

In such a crisis as this it is important that every effort should be made to conserve raw materials and to ensure that they are exploited to the full. Waste of valuable raw materials is often due to lack of knowledge and appreciation of the insidious nature of protein deterioration causing loss of output and a serious lowering of quality. This book is planned and written more as a primer for the practical man than an enlightened and original book for the research chemist, although it is hoped that the chemist will find it not without interest. The literature on glue and gelatine has not yet been swollen to undue proportions and it is hoped that this new volume, slim as it is, will prove a useful addition to the technical library as it caters on broad lines for all branches of the industry: raw materials, manufacture and application.

In Nazi Germany more importance has been and is attached to the so-called by-product industries than in the democratic countries. Waste of raw materials has, under the rigid discipline of National Socialism, come to be regarded as nothing short of sabotage of the country's effort. It is not advocated that such drastic measures should be adopted in the United States, but the need for a greater economy of our natural resources becomes ever more urgent.

To ensure an overwhelming flow of the vital munitions of war, every branch of industry must be made to contribute its full quota. In those cases where industries are interrelated this means that there must be full co-operation and the pooling of specialized knowledge and experience. The leather industry is intimately linked up with the glue and gelatine industry which itself is loosely tied to the stockyards and the hide and skin trades. Research, which is carried out in one branch of this industrial confederation, does not, as yet, benefit as it should the other branches. This is a confession of weakness and as such should be corrected so as to maintain the highest degree of industrial efficiency.

The hide and glue industry which has been geared to a peacetime industrial system with a predictable requirement takes some time to re-orientate itself so that greatly augmented wartime industries are kept supplied. The difficulties are immense and cannot be solved by mere price control or priorities. Ability to solve problems of output can only be ensured if there is the maximum co-operation between all branches of the industry and if knowlege is shared and experience pooled.

This book is just one small contribution to that effort to share knowledge and it is hoped that the information released may be some practical value to the industry and thus, in a small way, bring nearer the victory which we know is certain.

PAUL I. SMITH

CONTENTS

CHAPTER PAGE

PREFACE iii

I. EARLY HISTORY 1

II. INTRODUCTION TO HISTOLOGY OF SKIN AND FIBRE STRUCTURE OF PROTEIN 4

III. INTRODUCTION TO CHEMISTRY OF PROTEINS 14

IV. THE RAW MATERIAL FOR GLUE AND GELATINE 21

V. PRELIMINARY PROCESSES 35

VI. EXTRACTION OF GELATINE FROM GLUE STOCK 44

VII. FILTRATION, CLARIFICATION AND ADDITION OF CHEMICALS 61

VIII. EVAPORATION 69

IX. RECOVERY AND PURIFICATION OF BONE FAT AND SKIN GREASES 79

X. PROPERTIES AND QUALITIES OF GLUE AND GELATINE 86

XI. PLASTICS FOR GELATINE PLANT CONSTRUCTION 95

XII. GLUE AS AN ADHESIVE AND MISCELLANEOUS APPLICATIONS 99

XIII. GELATINE FOR THE PHOTOGRAPHIC INDUSTRY 107

XIV. GELATINE IN THE FOODSTUFF INDUSTRY 115

XV. MISCELLANEOUS APPLICATIONS OF GELATINE 123

INDEX 143

CHAPTER I

EARLY HISTORY

IT IS impossible to state with any degree of accuracy when it was found that a powerful adhesive could be made from pieces of hide and skin by boiling them in water, but like many other discoveries it was no doubt accidental. Bogue, "The Chemistry and Technology of Gelatine and Glue," refers to a period over 3,300 years ago when Egyptian cabinet makers used glue.

"Among the stone carvings of the ancient city of Thebes, of the period of Thothmes III, the Pharaoh of the Exodus, and at least 3,300 years ago, is one representing the glueing of a thin piece of rare wood of red colour to a yellow plank of sycamore." Various Egyptologists have shown that glue was in common use in Ancient Egypt. Dr. Howard Carter, "Tut-ankh-Amen," describes the finding of a specimen of glue in one of the tombs. "Glue," writes Dr. Carter, "was well known in Ancient Egypt, and a specimen recently examined may be described. This was found some years ago by myself in a rock chamber over the mortuary temple of Queen Hat-shep-sut at Dier el Bahari; it had been cast and was originally rectangular in shape, but now it is shrunken and distorted owing to desiccation; in appearance it cannot be distinguished from modern glue and it still responds to the usual tests."

In the tomb of Tut-ankh-Amen there is a large cedarwood casket, inlaid and veneered with ivory and ebony, which shows that glue was used for practically the same purposes as at the present time. It was also mixed with oils and pigments and used as a kind of paint. Gesso was a special form of plaster made up of whiting and glue and used for covering wood before gilding. There seems to be little doubt that the Ancient Egyptians were well acquainted with the manufacture and properties of glue; probably their acquaintance with it extends over four or five thousand years. Other ancient civilizations were also alive to the possibilities of a powerful adhesive being made from hide and skin waste. Authorities claim that in China during the seventh, eighth and ninth centuries glue was used in the manufacture of furniture.

From the earliest periods of civilization glue has apparently been known and renowned as an adhesive and repeated references to it are to be found in the classics, starting from Lucretius and Pliny and concluding with the great Elizabethan dramatists, Shakespeare and Marlowe.

Early methods of glue making were naturally very crude and simple. Pieces of hide and skin, with the hair removed, were boiled in a large vessel over an open fire, and the cooking continued until all the protein had dissolved. When the evil smelling liquid reached a suitable viscosity the vessel was removed from the source of heat, grease and hair skimmed off the surface and the gluestock liquor allowed to cool. It was then strained and poured out into rough stone moulds to dry. Naturally methods of manufacture differed enormously but they were all jealously guarded by the particular craftsmen who prepared the adhesive for their own use. Differences were, of course, detected in the respective abilities of the various types of hide and skin to produce good glue. Even in the time of Lucretius, 50 B.C., it was noticed that glue made from mature hide was superior to other varieties: "Materials are made one from bullish glue."

Glue was manufactured to considerable extent on the Continent of Europe during the seventeenth century, but it was not until the eighteenth that the industry sprang up in the United Kingdom. Since that time it has advanced steadily throughout the world but particularly in the United States. The finest grades of photographic gelatine, the purest and most difficult to product, but necessary in the manufacture of sensitized photographic material, are manufactured in the United States for both domestic and foreign use.

The advances which have been made during the present century in the production of glue can generally be traced to the scientific research carried out by the photographic and food industries. The actual methods of making common hide glue for the woodworking industry do not differ appreciably from the primitive procedure adopted by the Ancient Egyptians, but there are today available very many modifications of ordinary hide glue and a far greater standardization of quality.

CHAPTER II

INTRODUCTION TO HISTOLOGY OF SKIN AND FIBRE STRUCTURE OF PROTEIN

IT IS convenient to consider skin as consisting of two distinct layers: the epidermis, i.e., that thin layer of epithelial tissue lying on the true skin or derma, and the derma, corium or true skin itself. Underneath the corium is, of course the adipose tissue or flesh. The covering or epithelial tissue is made up of living epithelial cells, which, devoid of any blood vessels of its own, depends for nourishment on the absorption of blood and lymph from the derma which is fed by its own intricate system of blood vessels. As the living epithelial cells are pushed further away from the derma they become flattened out and eventually dry up to form a scaly layer which is worn away by body friction. This process of attrition continues throughout life.

The epidermis may, therefore, be considered as made up of the following layers, which are not distinct but interrelated:

Stratum corneum
Stratum lucidum
Stratum granulosum
Stratum mucosum
Pars papillaris.

The stratum corneum is the dry scaly layer, so-called dandruff on the human scalp, and represents old and dehydrated cells pushed upwards during growth from the lower layers. The stratum lucidum consisting of the protein eleidin is a transparent layer lying directly on the granular and pigmented cells of the stratum granulosum. The stratum mucosum or Malpighian layer of the epidermis is intimately connected to the derma by means of very fine nerve fibres. Pars papillaris consists of pattern-like protuberances of the actual derma into the epidermis.

Hair and sebaceous and sudiferous glands are all part of the epidermal co-system and are formed by the reproduction of epithelial cells. The orientation of these cells from soft and well nourished protoplasmic entities to elongated and hard structures so characteristic of the stratum corneum is also typical of the growth of hair.

The root of the hair passes below the epidermis into the derma and it is there nourished by means of the blood vessels of the papilla. Attached to each follicle is a system of sebaceous glands for lubricating the hair fibres and also protecting the skin against a drop in temperature.

Fatty exudations from the sebaceous glands cause the epidermal layer of the skin to become resistant to the penetration of moisture and saponification of these oleaginous materials is a necessary preliminary to the removal of the epidermis.

The epidermal structures consist of keratin which is removed by hydrolysis. It is the collagen and elastin, main constituents of the true skin, which are of prime interest to the glue manufacturer. These fibres lie, as stated previously, between the epidermis and the connective tissue or flesh. The dividing layer between the true skin and the epidermis consists of a very fine collagen layer, known as the grain or thermostat layer, whilst near to the flesh the fibres become more coarse and more plentifully interspersed with dark thread-like elastin fibres; this lower layer is usually known as the reticular layer.

It must not be thought that the structure of the skin is the same for all animals, fish, etc. Whilst in the main the general principles are the same, in detail, there is a good deal of difference. In the sheepskin, for instance, the proportion of fat cells to collagen fibres is much greater than in hides of calf or goat. Fish skins differ markedly from all animal skins as they do not possess any definite thermostat layer and instead of the characteristic interlacing structure of collagen fibres these are in ribbon-like formation running parallel to the surface of the skin.

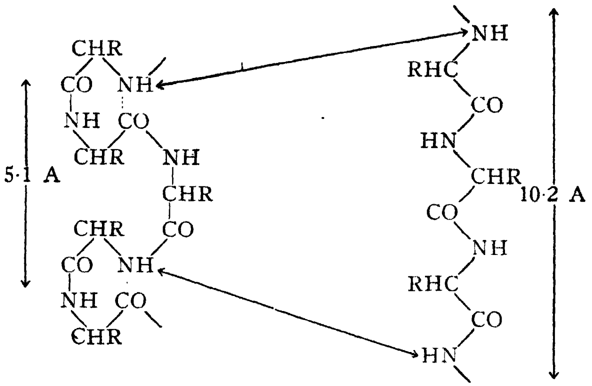
FIBRE STRUCTURE OF PROTEINS

The study of fibre structure has been given a great impetus by the research work carried out by Astbury, Woods, Grassman, Cherbuliez, Jeannerat and Meyer, Harrison, Speakman and Stoves, Highberger and Kertein, etc. Due mainly to Astbury and his co-workers through the development of X-ray diffraction photography an hypothesis has been evolved, which provides a logical and practical explanation of the main differences between the main animal protein fibres, collagen, elastin and keratin, and the changes which take place when these are subjected to heat, hydrolysis and other forms of chemical attack.

Astbury found that by stretching animal hair (keratin) in an atmosphere of steam he was able to change or re-orientate its chemical structure. This change is shown diametrically below.

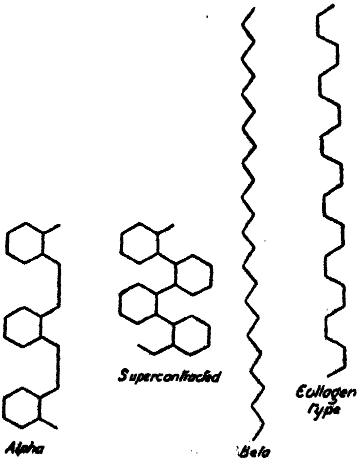
It will be seen that disulphide links are ruptured and the chains unfolded by the physical treatment afforded. Astbury was also able to contract the alpha keratin and so obtain the so-called super contracted form.

The structure of collagen in relation to keratin has been



The unfolding of an alpha keratin structure (left) to the beta form (right), according to Astbury . . .

shown by X-ray evidence to be somewhat intermediate between the beta form and the alpha form. Astbury (Trans. Faraday Soc. 34, 378 (1938)) has suggested the following forms as representing the four states of fibrous proteins.



The four principal states of fibrous proteins, according to Astbury . . .
(The alpha is represented by keratin structures; supercontracted by elastin, contracted muscle, hair shrunken in steam; beta, stretched hair and wool; collagen type, tendon, connective tissue and collagen fibres generally.)

The relationship of these basic fibre structures is of the greatest interest and importance to the glue manufacturer. The structures are by no means independent and have been shown by several workers to be reversible. Collagen fibre when heated in water to about 65° C. will shrink to one third of its original length and possess the physical properties of the elastin type fibre. A contraction of this nature is claimed to be due to the changes consequent on a balancing of electrical forces.

It will be seen from the above that changes in these main protein fibres are due to the folding and unfolding of long polypeptide chains. Astbury claims (Comt. Rend. Trav. Lab. Carlsburg. Ser. Chim. 22, 45 (1938)) and (Science Progress 34, 1 (1939)) that there is no real distinction between the fibrous and non-fibrous proteins or mucins, albumins and globulins, but that the fibrous are a denatured form of the non-fibrous.

Highberger states that the "process of gelatinization is conceived of as the penetration of water into the large spaces in the structure, with increasing hydration of the groups on the polypeptide chain, until the forces holding the structure together are no longer sufficient and the chains break away from their orderly packed arrangement, becoming a disorganized mass of highly hydrated polypeptide chains."

Cherbuliez, Jeannerat and Meyer (Arch. Sci. Phy. Nat. 1937, 19. Suppl. 122) conclude that gelatinization occurs in two main stages:

1. Loss of crystalline structure of native fibre (collagen A) by action of solvent. This is reversible; resultant fibre being resistant to trypsin.
2. Formation of gelatine by hydrolysis (boiling in water).

They state that collagen B results from collagen A by partial hydrolysis and is partly attacked by trypsin.

EFFECT OF CHEMICAL AGENTS ON SKIN PROTEINS AND INFLUENCE ON NATURE OF GELATINE

The general principles discussed in this chapter will, in the main, be later dealt with under separate headings in relevant parts of the book. It is, however, thought desirable as an introduction to practical considerations of manufacture to consider the matters coming under this chapter heading in greater detail than is possible later on.

At the outset, it can be said that there are a large number of different types of glue stock, many types being quite separate as regards character of skin protein, method of preservation, etc. The following list, which is by no means complete, gives some idea of market classifications:

1. Green salted hide trimmings, including green salted pates, green salted tips, and cattle pieces.
2. Limed cattle tail pieces and trimmings.
3. Goat trimmings and pieces, including long haired, short haired and dehaired.
4. Limed calf trimmings and pieces, including calf trimmings, green limed calf.
5. Coney stock.
6. Goat and sheep fleshings.
7. Packers trimmings, including green salted ears, lips, snouts and tails and green salted sinews and pizzles.
8. Sheep trimmings, including limed sheep trimmings.
9. Pickled sheep.
10. Horse fleshings.
11. Calf fleshings and horse and beam trimmings, including salted horse trimmings.
12. Sole leather fleshings.
13. Sulphide fleshings and kip fleshings.

14. Chrome stock, including chrome splits, chrome shavings and chrome trimmings.

It will be seen from the above that all these different types have been preserved or chemically treated in certain distinct ways—how does such treatment affect the protein matter and its eventual conversion into high grade gelatine?

In the case of wet salting, provided this has been carried out properly using at least one quarter of the weight of skins, there is no noticeable degradation of the protein, although, if the skins have been kept in the salted condition for a long time a certain amount of dehydration occurs resulting in a shrinkage of the collagen fibres and some difficulty might be experienced in effecting gelatinization by boiling. There is some evidence that during long storage in a salted condition active groups of the protein enter into combination with the salt and this means that a lowering of the glue-making quality of the protein takes place. It is, perhaps, also worth noting that salt stains may also show up rather badly where denatured salt is used. Stock which has been affected in this way is to be viewed with suspicion.

Where salt and acid, i.e. pickle, have been used for preserving the stock, there is a more drastic change in the protein fibres. During prolonged storage of pickled goods there is an increase in the opening up of fibres due to weakening of the reticular tissue around the fibres and fibrils. The former become shrunken due to dehydration of the skins. The disposition of the fat present in the skin also changes and there is a migration of the natural greases throughout the skin area instead of segregation in the restricted area of fat cells. This change in the disposition of the fat is not, in itself, harmful but the writer considers that it has a tendency to increase the greasiness of the resultant gelatine by rendering the fat more difficult to separate and collect.

Whereas there is little breaking down of the protein by hydrolysis during salting, provided this has been well carried out, there is a definite hydrolytic action when skin protein is soaked in lime water. Actual swelling begins at pH 12.5. The controlled physical action consists mainly of a separation or loosening of the fibre bundles without injury to the individual fibres. John H. Highberger and Herbert C. Stecker (Amer. Leath. Chem. Assoc. Journal, July, 1941) carried out a quantitative study of the formation of ammonia and urea during the liming of purified collagen. They showed that urea is definitely formed, due presumably to the hydrolysis of the guanidino groups of arginine and that its amount increases with time and with increased alkalinity of the solution. The major shift of the isoelectric point of limed collagen is claimed to be due to the hydrolysis of the acid amide groups with the formation of ammonia and new carboxylic groups. All of the acid amide groups are hydrolized in 4 days at ordinary temperature at pH 13.11. The amount of ammonia produced corresponds closely to the aspartic acid content of the collagen.

The introduction of caustic soda or sodium sulphide into the lime liquor results in a noticeable increase in swelling and hydrolysis.

According to Loeb (Proteins and the Theory of Colloidal Behaviour, 1924) the difference between the swelling of collagen fibres in solutions of caustic soda and calcium hydroxide is due to the difference in valency. Above pH 10–13 hydrolysis increases with great rapidity and there is a steady loss of valuable glue-making protein. The glue manufacturer classes sulphide fleshings lower than limed fleshings.

Whilst discussing the action of liming on the skin protein it is of interest to digress for a moment and consider the difference in the properties of gelatine made from limed and acid swollen stock. E. C. E. Hunter and A. J. Turner, (Trans. Farad. Soc. 36, 835 (1940)) found the isoelectric point of gelatine from acid swollen ossein to be between pH 5.5 and 6.5 and pH 4.9 to 5.1 for alkali swollen gelatine.

S. E. Sheppard, R. C. Houck and C. Dittmar, (J. Phy. Chem. 44, 185 (1940)) determined the sorption of water vapour by dry gelatine and its electrical conducivity at various degrees of relative humidity. Little difference was found in the absorption value of lime processed gelatine (isoelectric point pH 4.8) and acid processed pigskin gelatine (isoelectric point pH 8.2) until the vapour pressure approached saturation when the lime processed material showed greater absorption. The moisture regain was found to decrease with the pH of the gelatine solution (at coating) but no minimum was found at the isoelectric point. Highberger, (J. Amer. Chem. Soc. 61, 2302 (1939) has determined the isoelectric point of collagen prepared from steer hide with only a mild alkaline treatment. The micro-electrophoretic technique of Abramson was used. The isoelectric point of this material was located, very surprisingly, at pH 7.8. The conclusion was drawn that the action of lime, or any severe alkaline treatment, produces a chemical change in the collagen, the effect of which is to lower its isoelectric point (and that of gelatine made from it) from pH 7.8 to around pH 5. Beek and Sookne (J. Amer. Leather Chemical Asso. 34, 641, 1939) attribute the change in isoelectric point on alkaline treatment to hydrolysis of amide groups, in which case ammonia is liberated and free acid carboxyl groups formed in the protein, the net effect of which is to lower the isoelectric point of the collagen (and that of gelatine made from it).

Gelatine made from limed stocks and subsequently swollen by further liming shows a lower isoelectric point than gelatine made from green or salted stock and subsequently limed.

There does not appear to be any noticeable lowering of the pH of stock which has been limed with solutions sharpened by means of caustics when compared with stock swollen in ordinary straight lime liquors. The chief objection to the use of caustic soda or sodium sulphide in the preservation of stock is that hydrolysis and therefore degradation of the protein matter is increased beyond all control if the pH exceeds 10–13. At a time such as the present, when waste must be entirely eliminated, it is of the utmost importance that loss of glue-making protein by intensive hydrolytic action should be avoided at all costs. By employing fresh gluestock the manufacturer increases his yield and also produces a higher grade product. In those cases in which gluestock has to be preserved preservation should be planned so as to ensure minimum loss or deterioration.

In relation to chrome shavings and trimmings, etc., it is suggested that the tanner might well detannize this material himself as it is easier to treat when fresh than when stale and dry. De-chroming is, in the light of the latest research, a comparatively simple matter and may be carried out very successfully by processing the shavings in weak solutions of borax, sodium bicarbonate, sodium hydroxide, triethanolamine, organic acids and their salts. Use of a small quantity of a good wetting agent helps materially in the softening of chrome tanned leather and thus facilitates its conversion into valuable gluestock.

CHAPTER III

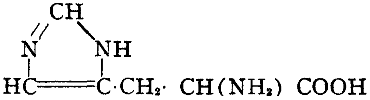
INTRODUCTION TO CHEMISTRY OF PROTEINS

IT IS not proposed in this brief introduction to delve deeply into the more abstruse theories, but rather to give a simple and concise account of the chemical constituents of the protein matter which forms the basic raw material for glue. The glue manufacturer is mainly concerned with collagen which is, of course, the basic constituent of animal and fish skins. This protein, which is closely akin to gelatine, is an exceedingly complex organic material containing carbon, hydrogen, nitrogen and oxygen. Some idea of its complexity is given when it is stated that according to Highberger J. A. C. S. 61, 2302, 1939, the molecular weight is 34,500.

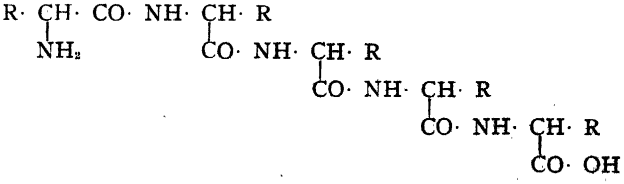
When collagen is broken down by hydrolysis or continued boiling in acid or alkaline solution it is found by analysis that the complex protein molecule is broken down step by step into simpler bodies:—proteoses, peptones, polypeptides, amino acids and finally ammonia. It is estimated that something like 24 amino acids are present in the original protein. The following table given by F. Schneider. Colleg. 839, 97 (1940) gives a fairly clear idea of the main amino acids isolated from collagen.

	PERCENTAGE OF TOTAL NITROGEN		MOLECULAR PROPORTIONS	
	Found	*Calculated*	*Found*	*Calculated*
Glycine	26.8	27.4	8.	8
Remaining mono-amino acids	26.2	27.4	7.9	8
Proline	13.1	13.7	3.9	4
Oxyproline	6.4	6.8	1.9	2
Arginine	14.6	13.7	1.1	1
Lysine	5.3	6.8	0.8	1
Histidine	0.8			
Amide N	4.2	4.2		
	97.4	100.0	23.6	24.0

The simplest amino acid is glycine, aminoacetic acid, $NH_2 \cdot CH_2 \cdot COOH$ and one of the most complex is histidine, β-iminazolyl-α-aminopropionic acid.



These amino acids can, under certain conditions, be made to combine to form chain like compounds known as polypeptides. Emil Fischer in the early part of the century was able to synthesize a complex peptide by combining the amino-group of the amino acid with the carboxyl group of another. The now familiar polypeptide is thus built up as follows:



The most complex peptide synthesized by Fischer was an octadecapeptide but so far it has proved impossible to prepare in the laboratory a protein-like body identical with a natural one owing, apart from other difficulties, to the very large number of different arrangements or isomers possible in building up the polypeptide.

Schneider is of the opinion that the collagen values are in keeping with a simple molecular proportion between the most important amino acids, and hence with a periodic repetition of the single acids along the polypeptide chain of the molecule as suggested by Bergmann for gelatine in 1935. He suggests that every third acid in the chain is glycine, every sixth proline, every twelfth oxyproline, and every 24th lysine or arginine. Schneider tabulates the most important amino acids within the period of 24 acids and presents the following simplest formula:

G—M—P—G—M—X—G—M—P—G—M—X
G—M—P—G—M—X—G—M—P—G—M—X

In the above formula G is glycine, P is proline, M other amino acids and X is twice oxyproline, once lysine and once arginine. The eight mono-amino acids are written the same since nothing is definitely known about their periodicity which is certainly greater than 24.

Support of the above theory is afforded to some degree by analysis of some of the peptides isolated from gelatine hydrolytic products. A formula given by Schneider which fits as much as possible all known results

Lys—P—G—M—OP—G—M—P—G—M—M—G
Arg—P—G—M—OP—G—M—P—G—M—M—G

harmonizes with isolated lysylprolylglycine.

Gelatine is the first degradation product of collagen and it is suggested by Hofmeister, Z. physiol. Chem. 2 (1878) 299, and corroborated by Plimmer that collagen is an anhydride of gelatine. Emmett and Gies suggest that the conversion of collagen into gelatine involves an intramolecular rearrangement. This latter view would appear to be supported by the recent radiographs of I. I. Sokolov, Colloid Journal, U.S.S.R. 1940, *6*, 99.

CHEMICAL COMPOSITIONS OF GELATINE AND COLLAGEN

	GELATINE		COLLAGEN	
Amino Acid	*wt. %*	*Percentage N*	*wt. %*	*Percentage N*
1. Glycine	25.5	26.4	24.7	25.6
Glycine plus Serine	26.4			
2. Alanine	8.7	7.6		
3. Leucine	7.1	4.2		
4. Phenyl Alanine	1.4	0.7		
5. Tyrosine	0.4	0.2	1.0	0.4
6. Serine	0.4	0.3		
7. Methionine	1.0	0.6		
8. Aspartic Acid	3.4	2.0	5.75	3.0
9. Glutamic Acid	5.8	3.1		
10. Proline	19.7	13.3	18.9	12.8
11. Oxyproline	14.1	8.3	10.8	6.4
12. Arginine	8.2	14.7	8.4	15.0
13. Lysine	5.9	6.3	4.7	5.0
14. Histidine	0.9	1.35	0.6	0.9

The above table gives a good idea of the importance of the amino acids in the build-up of gelatine and collagen. The results are obtained by a number of workers and they are not expected to compare arithmetically with the table reproduced at the commencement of the chapter.

HYDROLYSIS OF HIDE PROTEINS

It has previously been pointed out that hide proteins can be broken down into simpler compounds by means of hydrolysis which is a reaction of the greatest importance to the glue manufacturer. Gelatine is formed when collagen is dissolved or solubilized by cooking or heating with water to 70° C. If hydrolysis is allowed to proceed beyond the gelatine-forming stage the protein becomes progressively less useful. Procter gives the following list of hydrolytic products of hide substance:

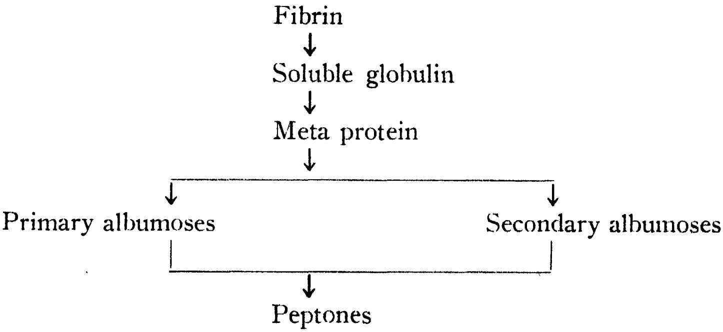
Protein (collagen, casein, albumin, etc.)
↓
Metaprotein (Lieber Kuhn's jelly)
↓
Proteoses (gelatoses, albumoses)
↓
Peptones
↓
Simple polypeptides (kyrins)
↓
Amino acids

Whilst water itself will hydrolize collagen the best known and most rapid hydrolytic agents are:

Sulphuric acid
Hydrochloric acid
Baryta water
Hydriodic acid
Lime water
Caustic soda

The glue manufacturer has to remember that hydrolysis must be most carefully controlled, otherwise there will be serious deterioration of the gelatine. Continued boiling beyond the optimum point produces thermal denaturing which degrades the useful properties of gelatine and renders it less valuable for all technical purposes. I. I. Sokolov, Colloid Journal, U.S.S.R. 1940, *6*, 815, states as mentioned previously, that thermally denatured gelatine (soluble) peptizes normal (insoluble) gelatine. It is suggested by Sokolov that in denatured gelatine, intramolecular changes occur with the resultant formation of ring structures in place of the chains characteristic of unprocessed gelatine. There is an increase in the porosity of gel in the case of denatured gelatine.

Apart from hydrolysis induced by chemical reagents various enzymes, e.g. trypsin, pepsin, have the power of breaking down collagen and gelatine, provided conditions, particularly pH, are suitable. (Trypsin requires an optimum pH of 5.9.) It has been shown by Thomas and Seymour-Jones, J. Amer. Chem. Soc. (1923), that trypsin will effectively hydrolyze collagen even when the latter is not swollen with either acid or alkali. The ability of enzymes to hydrolyze proteins is well typified by the following simple diagram made by Cole which shows the degradation of fibrin by means of pepsin:



Hydrolysis of gluestock takes place alongside putrefaction. Abt (Journ. Soc. Chem. Ind. 1906, 109) gives the following table illustrative of the action of putrefactive organisms:

Aerobic	Mixed	Proteolytic:	Micrococcus flavus liquefaciens, protens vulgaris, white staphylococcus.
		Peptolytic:	B. Coli, B. filiformis, streptococcus pyogenens, diplococcus grisens.
	Simple	Proteolytic:	B. subtilis, B. mesentericus.
		Peptolytic:	Protens zenkeri.

Anaerobic	Mixed	Proteolytic:	B. perfringens, B. bifermentans sporogenens.
		Peptolytic:	B. bifidus, B. lactopropylbutyricus non-liquefaciens (Tissier).
	Simple	Proteolytic:	B. putrificus, B. putidus gracilis.
		Peptolytic:	Diplococcus magnus anaerobinus, B. faecalis alkaligenes.

CHAPTER IV

THE RAW MATERIAL FOR GLUE AND GELATINE

THE bulk of the glue manufacturer's raw material consists of hide proteins purchased direct from the tanner. It has to be remembered that whilst this offal is a by-product to the tanner it is a basic raw material to the glue manufacturer. This fact is not always appreciated and yet it is necessary to assess rightly the fundamental difference in outlook between the two manufacturers. Prior to the war, tanners did not, as a whole, detail ways and means of retaining the freshness of offal and its suitability for glue and gelatine manufacture. This indifference was due primarily to the following main factors:

1. The price of offal was small.
2. The requirements of the glue manufacturer translated in tonnage of offal varied quite considerably.
3. Ignorance or indifference regarding the deterioration of the hide proteins due to putrefaction and hydrolytic changes brought about by improper or prolonged storage at the tanyard.

In the past the tanner has often failed to realize that although his main object is the manufacture of leather, it is very much to his advantage to make his by-products contribute largely towards the maintenance of the plant. As gluestock is one of the most important of these products he would do well to study at some length the ways and means of retaining its freshness and suitability for high grade glues. By keeping his hide and skin offal in a sweet condition, the tanner not only ensures a better, and therefore more profitable market, but also eliminates some of the bad smell with which a tanyard is usually associated.

When a large heap of hide and skin pieces is left exposed to the weather for any considerable time, those pieces on the top become bone-dry and assume an objectionable bluish color which gives the buyer a bad impression. In addition there is also a considerable loss in weight due to drainage of the stock. As the offal is always sold by weight this diminution, which may be as much as 20%, represents a serious pecuniary loss to the tanner. It is also worth noting that stock which has been allowed to become dry and discolored is not so easy to process in the glue factory as the normal consignments.

It is a good practical suggestion to have the "spetches," common British term, turned over with a fork about once a day so that the weight can be kept more or less constant and risk of discoloration thereby greatly diminished.

The tanner is sometimes confronted with the fact that the glue manufacturer through bad trade or other causes, cannot deal with the whole of his stock, with the result that a considerable amount of highly putrescible material collects in the tannery. A satisfactory solution of this problem is difficult to obtain. Some tanners attempt to overcome the difficulty by sprinkling lime water over the hide and skin pieces two or three times a week and turning them over fairly regularly. This method is useful in so far as breakdown of the proteins through intensive hydrolytic action is lower than is the case when the offal is immersed in lime liquor. On the other hand the labor charges are unduly heavy and the area needed for spreading out the pieces is large and may prove a source of inconvenience. Deterioration due to bacterial activity and action of proteolytic enzymes may be prevented by the addition of small quantities of disinfectants to the weak lime liquor or by regulating the pH so that it is about 12. It should, however, be remembered that even if the activities of undesirable organisms are reduced to a safe minimum, hydrolytic action will continue and the glue making properties thereby reduced. The author has found by experience that hide and skin pieces have a tendency to become "meally," that is, they appear to lose their characteristic "fleshy" nature and can easily be broken up into powder or meal by rubbing. This peculiar material is not of much value to the glue manufacturer.

It has been shown by I. I. Sokolov, Colloid Journal, U.S.S.R. 1940, *6*, 815, that denatured gelatine, i.e., gelatine boiled for 60 hrs. under reflux, differs fundamentally from normal gelatine, as during thermal denaturing intramolecular changes occur with the resultant formation of ring structures in place of the chains characteristic of unprocessed gelatine. On addition of the denatured gelatine to normal gelatine there is some peptization and degrading of the jelly through porosity. The above fact is important because it has been suggested that intensive liming or storage in a saturated condition brings about somewhat similar changes in the collagen. The presence of additives, e.g. soda ash, sodium sulphide, caustic soda and ammonia formed during degradation of proteins all tend to increase the rate of protein deterioration. J. A. Wilson, "Theories of Leather Chemistry," J. Amer. Leather Chem. Assoc. 12 (1917) 108, suggested that "barium and calcium hydroxides hydrolyze proteins to a lesser degree than the hydroxides of sodium or ammonium because of the higher valency of the cations. The swelling of proteins in alkaline solution is due to the pull of the cations of the protein salt, which tend to diffuse from the region of high concentration of ions in the jelly to the region of lower concentration in the surrounding solution. If this pull is sufficiently great, we might reasonably expect a breaking up of the units making up the protein jelly. A sodium or ammonium ion exerts its entire pull upon a single unit, whereas the pull of a divalent cation is divided between two units, making the tendency towards decomposing the protein only half as great."

There is another method of preserving the hide and skin offal which is usually carried out only for the finest material, i.e., hide bellies and other high grade offal for the manufacture of photographic gelatine. This is drying. The advantages of this means of preventing deterioration are:

1. Bacterial or putrefactive agencies rendered generally ineffective.
2. Chemically induced hydrolytic decomposition checked.
3. Reduction in weight and lowering of freight charges.

Against the apparent advantages must be weighed the following disadvantages:

1. The method is fairly expensive to carry out as it involves high labor charges. The cost cannot be justified for any but the finest grades of protein matter.
2. In the case of some classes of hide or skin waste, drying causes a serious lowering of quality. D. Rossetti, Boll. della Staz, Esper. per l'Ind. dei Pelli, 18, No. 7, 57, 1940, states that on drying hide fleshings there is a very serious discoloration, particularly where the fat-content is high. He gives the following useful data regarding the difference in the skin fat extracted from wet and dried fleshings:

	WET	DRIED
Color	*Ivory white*	*Dark maroon*
Density at 20° C.	0.910	...
Iodine No. of fat	65.1	...
Iodine No. of liquid fatty acids	89.8	...
Acid No.	4.64	4.74
Unsaponifiables	3.40	7.90
Oxidized fatty acids	trace	9.40
Titer	34.6	...

It will be observed that the difference between the two fats is marked and the drop in the market value of the fat from dried fleshes is of importance to the glue manufacturer who naturally calculates to sell his recovered fats at a reasonable profit. Dried fleshes are difficult to soak back and process in the glue works.

Summing up, it can be said that where there is a constant flow of glue stock from the tannery to the glue factory the best condition is that obtained by spreading out the limed pieces and turning them over at regular intervals. For the highest grade gelatine-making stock which has to be sent in regular consignments to the plant probably a long distance away (a great deal was sent from the United Kingdom to the U.S.A. before the war), drying under the most careful conditions can be recommended as it ensures complete cessation of all decomposition changes and makes available to the glue manufacturer a product of great potential value.

The following notes relate to the most important types of hide protein:

CALFSKIN

From this source the glue manufacturer obtains the material for some of the best and clearest gelatine and glue. The pates and trimmings, but not fleshings, from average sized calfskins are excellent for the manufacture of edible gelatine. Skins from very young animals contain appreciable quantities of water and mucin-like substances which lower the setting properties of the jelly. It is the usual practice to keep the trimmings or "roundings," pates and fleshings quite separate as they are priced differently, the best figure being obtained for the pates.

The majority of tanners store the roundings and pates piled up in small heaps covered with sacking which has been dampened with lime liquor. Fleshings are generally preserved in a weak solution of lime. This procedure is to be recommended, especially when the heaps are turned over with a fork once a day to ensure equal distribution of lime liquor. The reason why fleshings are rated lower than roundings is owing to the fact that the sub-cutaneous tissue does not yield such good quality glue as collagen from the skin proper. The fleshings also contain a relatively high proportion of fat, 4–6%; actual glue making protein being only 10–15%.

Calves' feet do not yield a large quantity of glue. They are, however, of special importance, being a source of neatsfoot oil.

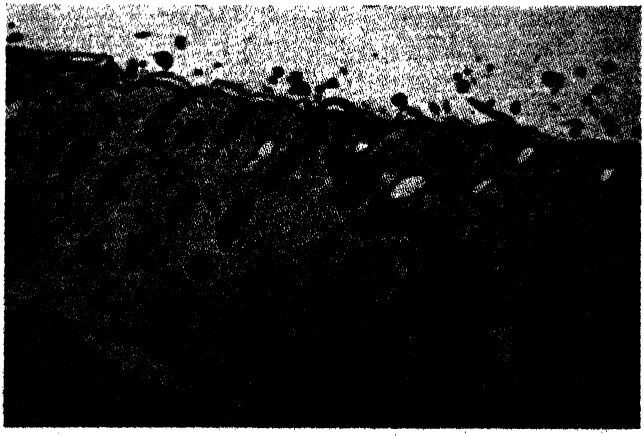


Photo-micrograph of transverse section of calfskin. This photograph shows epidermal structure, grain or thermostat layer and coarse reticular layer.

HIDE OFFAL

Under this heading are the trimmings, fleshings, feet, etc., and, as pointed out earlier in this chapter, limed bellies and hide offal for the manufacture of the finest photographic gelatine. Hide pieces are green, dry, dry salted, wet salted and limed. Wet-salted stock, such as that obtained from frigorific hides, is best soaked in clean cold water to remove the dirt and salt, then preserved in a weak solution of lime. This procedure applies equally well to dry-salted stock. Pieces from sun-dried or "flint dried" hides can be kept indefinitely, provided, of course, that they are stored in a dry warehouse. Roundings, etc., from limed goods are best preserved in the open air in the same way as calf and sheep stock. Fleshings may be safely stored in a large tub containing a weak solution of lime.

WASTE FROM SHEEPSKINS

Offal from the sheepskin forms a very important portion of the glue manufacturer's raw material. The first waste occurs when the skins are trimmed, i.e. the heads, tails and shanks or legs are cut off. These are known as roundings. At a later stage the flesh or sub-cutaneous tissue is removed, either by machine or by means of a special knife worked by normal labor over an almost perpendicular wooden beam. Some tanners press the fleshings and extract the valuable fats which they contain, and this procedure has been found more profitable than selling the material direct for glue. The residue obtained from the large hydraulic presses is quite unsuitable for utilization as glue stock, but it can be sold as a cheap nitrogenous fertilizer.

Sheepskin offal makes a good glue, but is inferior to either the calf or hide varieties owing to the large amount of natural fat present in the skin. D. N. Matrosovitch, Colloid Journal, U.S.S.R. *6,* 575 (1940), has shown that the sterols play an important part in the swelling of gelatine and the presence of impure cholesterol has a marked effect. It is suggested by the author that the above may be at least a partial explanation why glue from sheepskin offal, through excessive swelling and effect on the micelle structure does not possess the high adhesive properties of glue made from other hide proteins.

Before leaving the subject of sheepskin offal it should be mentioned that "Colty" or stale material is best kept apart from the fresh pieces.

PIGSKIN

In the United States considerable quantities of pigskin are used for making edible gelatine and glue. Generally speaking, the gelatine is not so suitable for those applications requiring the retention on dilution of the highest jelly strength, such as for the manufacture of marshmallows and for photographic emulsions. This does not mean to say that pigskin is an inferior raw material; on the contrary it gives a clear and sparkling gelatine or glue and finds many applications in industry. As the skin contains fairly large quantities of grease it is necessary extra care be taken to remove this from the glue liquor during extraction. The writer is of the opinion that acid swelling is preferable for pigskin instead of the usual alkali swelling and facilitates production of a high grade gelatine. This view is not, however, generally shared in the industry.

GOATSKINS

There is comparatively little waste from the average goatskin which only measures something like 6 sq. ft. per skin. The offal makes an excellent strong glue.

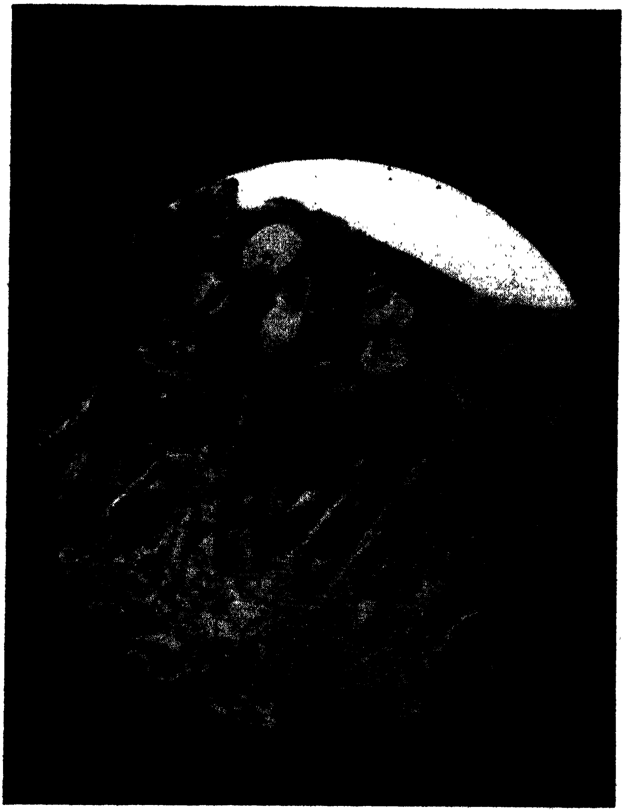


Photo-micrograph of raw goatskin (magnification 80) taken by the author. This transverse section shows hair roots, fat cells, pigments, nerves, elastin fibres, etc.

FURRIER'S WASTE

In the manufacture of men's hats there is a considerable tonnage of rabbit pelts made available for glue making as obviously only the fur is used for making hats and the pelts are of no value. Rabbit skin makes a good glue and is a valuable raw material, being easy to clean and process. Small pieces of furs, too insignificant to be of any value to the furrier, are generally sold direct to the waste merchant for disposal in convenient lots to the glue manufacturer. This waste is easy to de-tan as furriers do not tan their skins completely.

BONES

These contain something like 11–12% ossein; 15–16% fat; 20–21% mineral matter and 50–51% water.

The ossein consists of several complex proteins, the principal being collagen, and is of great value to the glue manufacturer, yielding a bright strong quality gelatine. Fresh bones contain a higher percentage of ossein than dry and aged specimens. This protein material is also an important constituent of horn piths. These are made up of two portions, one being composed of organic constituents and the other inorganic. Separation of one from the other is achieved in the plant by treatment with acids and continual washing of the ossein with running water. The fat from bones is extracted during the process of glue making or preparatory to it, and is known commercially as "bone fat," large quantities of which are sold to soap and lubricating manufacturers. Bone oil is also obtained from bones. It is a heavy, dark brown liquid and when redistilled yields considerable quantities of pyridine bases and ammonia.

LEATHER SCRAP

A large amount of leather waste accumulates in the tanner's and boot manufacturer's plants and, in normal times, proves very difficult to dispose of unless the manufacturer himself has it taken away to a dump or burns it under his own boilers. Vegetable tanned leather wastes are practically valueless to the glue producer as the removal of tannin cannot be accomplished with any degree of satisfaction. Chrome tanned leather scrap may be profitably converted into gluestock, specially in wartime when the demand for adhesives cannot be satisfied and all types of raw materials, no matter how uneconomical, have to be utilized.

Detanned chrome leather can make a reasonable commercial glue. Removal of the chrome content may be undertaken by use of 0.1 molar solutions of sodium bicarbonate, sodium carbonate, borax and oxalic acid as well as Rochelle salt (potassium sodium tartrate) and the salts of other hydroxy-acids.

Chrome shavings, which are the most useful form of leather gluestock, must be kept damp as once they get really dry it is practically impossible to wet them down again. The best means is to stock this material in large tubs or vats and to water it every two or three days and disturb the mass with a fork. It is a good practice to throw some wet sacks over the tubs in the summer months.

The shavings or scraps of full chrome leather can be detanned by merely soaking in a solution of Rochelle Salt 100° F. for 12 or more hours, stirring the material during the process. A better method is to suspend a cage containing the shavings in a pit or vat containing the detanning solution. The detanned leather can then be washed and processed in the glue factory in the normal way.

It might be mentioned that there is some competition as to who shall use these chrome shavings in wartime. They are valuable as a reducing agent; 250 lbs. of shavings, moisture content 58%, will reduce 100 lbs. bichromate of soda.

Fish Waste

Waste from large fish canneries, floating whale and shark factories, markets and wet fish shops, etc., is utilized to a large extent in the manufacture of glue and gelatine. The essential glue-making material is the same as with animal offal, namely collagen which, in the form of ribbons running parallel to the surface, makes up the bulk of the skin. Sebaceous or fatty glands are present in fish skin in great abundance and there is, in consequence, a large proportion of fat to recover in glue making. Great strides have been made in Japan in the utilization of shark skin for high grade gelatine and it is claimed that excellent photographic gelatine may be prepared from this source. S. Kikuti (J. Soc. Chem. Ind. Japan, 1939, *42*, 370–71 (b)) claims that gelatine prepared from dried shark skin has a nitrogen content of 16.9% N. Its 10% gel melts at 29.5° C.; solidifies at 23.3° C. and has (Redwood) 47.6 and gel strength 237 g; Kikuti states that the X-ray diagram of shark gelatine is identical with that of Nelson gelatine.

DISTINCTION BETWEEN GLUESTOCK AND GELATINE STOCK

As suggested before, similar materials are used in the manufacture of gelatine as in glue production—hide and skin offal, bones and fish waste all are utilized. In considering the process of gelatine production it must be realized that this substance ranks as an important food, and consequently the raw materials employed must conform to certain standards of purity not demanded for ordinary glues. Again, the conditions under which gelatine is made must conform to the very high standards of hygiene required for all food factories under existing Food Laws.

Only the very best hide and skin offal is utilized for gelatine. The presence of even small quantities of undesirable materials in a boiling of gelatine will lower the value of the resulting product to a considerable degree. Goat, sheep, hog and similar skin offal is not usually employed by manufacturers, owing to the difficulty of eliminating sterols and foaming agents.

Bones may be considered as an important source of gelatine, but here again there are difficulties in the way of selecting the most suitable materials. The dry and stale varieties, commonly known as junk bones, and the steamed and pickled specimens are totally unsuitable for edible gelatine. Soft bones from very young animals contain excessive proportions of water and consist entirely of a protein material practically identical with cartilage. They make, therefore, a rather inferior product and their use is not recommended when a really first grade gelatine is desired. Briefly it may be said that the best bones are from mature cattle but they should be treated or worked as quickly as possible. Long delays in boiling favor the growth of liquefying organisms which cause the protein matter to decompose.

ISINGLASS RAW MATERIALS

Isinglass is a much more expensive substance than gelatine and consequently the raw materials used for its manufacture are the very best and most suitable for the purpose. This well-known protein is made from the swimming bladders of the sturgeon, cat-fish, hake, cod, etc.

The sturgeon fisheries of the U.S.S.R. are of immense value as the fish can be utilized to almost 100%. The flesh is most acceptable as a food and is salted, smoked or dried for the purpose. Other valuable portions are the ovaries, which are made into caviar, and the air bladder removed from the carcass and preserved ready for the manufacture of isinglass. Various waste products obtained during the dissection of the body are boiled for the recovery of oil and also converted into fertilizers.

The sounds or bladders of the sturgeon and other suitable fish reach the manufacturer in two conditions—salted or air dried. Prior to treating or preserving the bladder the inner or glutin-containing membrane is removed. The salting is quite simple and in the majority of cases is performed by packing the sounds in large barrels and throwing on top of each layer a sprinkling of clean salt. The concentrated brine prevents any decomposition of the protein matter and may easily be removed by washing in water. Air drying, if carried out on proper scientific lines, is very satisfactory but, as often happens, bladders are flint dried through exposure to widely varying temperatures and, in consequence, prove extremely difficult to soften and work.

CHAPTER V

PRELIMINARY PROCESSES

PRESERVATION OF GLUESTOCK, WASHING, LIMING AND DELIMING

GENERAL METHODS OF PRESERVING STOCK PRACTICED BY THE GLUE MANUFACTURER

IN PREVIOUS chapters the general methods of preserving stock, such as hide and skin waste, fish and bone, offal, etc., have been outlined. Exactly the same means are employed by the glue technologist as by the tanner and the butcher, etc.

Those who have any knowledge of glue production know that a considerable surplus of raw material must be stored, in order to ensure continuity of manufacture. The preservation of this stock requires very careful consideration.

Stock from the tanner, which includes hide and skin pieces and fleshings, are already in a limed condition. In this case all that is necessary is to pile it in heaps and cover the surface with a layer of slaked lime. This is a better method than treating with lime-water. The technologist has to keep in mind the important fact that hydrolysis must be avoided if a good quality glue or gelatine is to be obtained. On no account should limed stock be allowed to remain intact for any lengthy period. If there is no possibility of early consumption, then the heaps should be raked up and more slaked lime added, but even this will not prevent serious loss through hydrolysis, if the material is not put into work as quickly as possible. Salting is frequently employed for the preservation of gluestock. The usual method of carrying out this operation is to spread the stock out on the concrete or brick floor and cover with a layer of salt. Add another layer of offal, then one of salt, and so on. Great attention should be paid to salting, as if the layers are not uniform, putrefaction will start, and the stock be damaged. It must be remembered that, if the raw material is allowed to deteriorate at this stage, it is quite impossible to apply any effective remedy at a later one.

Desiccation or the drying of the glue stock is practiced to a certain extent, especially in conjunction with light salting. If carried out on scientific lines it can be most efficacious. It should be borne in mind, however, that, if the drying has not been properly carried out, it becomes extremely difficult to soften the stock at a later process.

Proctor points out that, if the hide is dried at a high temperature, then the albumins present will coagulate, and thus be rendered insoluble. Eitner (Gerber, 1880, p. 112) gives the following table, which illustrates the above:

Sample	*Temperature of Drying*	*Remarks*	*Time of Softening in Water*	*Remarks*	*Dissolved by Salt Solution*
1.	15° C.	In vacuo	24 hrs.	Without mechanical work	1.68%
2.	22° C.	In vacuo	2 days		1.62%
3.	35° C.	In drying closet	5 days	Twice worked	0.15%
4.	60° C.	In drying closet	Refused to soften sufficiently for tanning		Traces

The majority of glue manufacturers make use of liming for partially-limed stock, and salting for green or partially-salted material, and these methods generally fulfill all requirements if carried out on the lines indicated.

In considering the important subject of preservation, the technologist must keep in mind the essential fact that "delay in working is fatal."

THE WASHING OF GREEN AND SALTED STOCK

This operation would appear to be exceedingly simple and unimportant, yet, as frequently happens, appearances are apt to be deceptive. The washing of the gluestock requires more than ordinary care, and considerable ingenuity has been exercised in designing special machines to effect complete washing.

Throughout the entire production of glue and gelatine the manufacturer is faced with difficulties, which are both original and spasmodic. This is not difficult to understand, when it is realized that the material dealt with is practically an unknown "x" and the constitution and properties of "x" are still a matter of conjecture.

Green stock may be contaminated with blood and dirt, in an early or advanced stage of putrefaction, or fresh. The object of washing is to remove all extraneous matter, blood, lymph and hydrolytic products produced by proteolytic micro-organisms. In order to achieve these results cold water should be used and the stock agitated during treatment. If warm water is employed, the washing may be more thorough, but there is grave danger of putrefaction, as gelatine-liquefying micro-organisms flourish at blood-heat. Some glue manufacturers use antiseptics when dealing with putrid or old stock. These must be handled with care as an excess of antiseptic body may interfere with the physical properties of the finished gelatine. Best known antiseptics are: phenol, orthonitrolphenol, sodium acid fluoride, para-cresol, formaldehyde, parachlorphenol, sodium salt of parachlormetacresol, para-nitrophenol, mercuric chloride, boric acid, beta naphthol and salicylic acid. Parachlormetaxylenol is a most effective antiseptic and may be used in very low concentrations; one part in 6,000 is capable of preventing the growth of putrefactive bacteria. Parachlormetacresol, which is soluble to the extent of 0.4 gram per 100 grams water is also an antiseptic particularly well suited for use in the soaking of glue stock. Phenol, soluble to the extent of one part in 15 parts water, is a reasonably cheap and harmless antiseptic. Strengths of 10 to 20 parts per 5,000 parts water are useful.

There are many washing machines in use by manufacturers, but it may be said that any plant is suitable which permits of free agitation of the stock in running water.

The most popular mechanical device for quickening up the soaking is the tumbler. This is simply a large barrel mounted horizontally on its axis, with baffles on its periphery to keep the stock from sliding. The stock and water are

Type of paddle used for washing gluestock in a British plant.

introduced through an opening in the side of the vessel, which is, of course, closed during rotation.

Paddles, complete with revolving blades and provided with a false bottom, are in common use in this country. By means of a stopcock the wash water is continually drained off, fresh water being added. They are very satisfactory, but the time taken for complete washing is somewhat longer than when the tumbler is used.

Other washing machines in use, both in England and America, are the hollander and cone mill, the latter being the more popular.

Bogue, "Chemistry and Technology of Gelatine and Glue," sums up the relative advantages of the various kinds of machines as follows:

> These four representative types (referring to the cone mill, tumbler, hollander, and half-round mill) may, to a certain extent, be used interchangeably. The cone mill, which produces a combination of rubbing, kneading and washing, can be used on almost any kind of hide stock. In the tumbler the pounding and kneading predominate, and it is therefore, more suitable for hard thick stock. In the hollander the rubbing predominates, and it is most serviceable for loosening foreign materials which adhere rather firmly to the fibres, but its construction prohibits use on heavy or non-uniform stock. The half-round mill gives a simple agitation and rapid circulation of water, suitable only for finely-divided and light stock.

Dealing now with salted stock, the washing must be carried a stage further. The proteins must be softened in just the same way as green material, and besides this, all traces of neutral salts removed, otherwise the liming process will not be carried to successful completion.

Chlorides are most undesirable in the glue stock during the later processes. The best method of ensuring the removal of all traces of salt is to test the wash water with silver nitrate. The washing should be continued until a sample of water gives no precitate with silver nitrate, making due allowance, of course, for the original chlorides present in the water.

LIMING

This is a very necessary process as unless the protein matter is properly swollen, the process of extraction or cooking is impeded and the quality of the resultant glue impaired. It is also important that certain of the protein matters in the hide substance should be solubilized by hydrolytic action. The presence of the mucins, albumins, globulins, etc., in glue is to be deprecated owing to the fact that they tend to lower the tensile strength of the glue film. By the action of weak alkali, these insoluble and semi-soluble proteins are rendered fully soluble and can later be removed completely by washing.

According to Stiasny, "Some Modern Problems in Leather Chemistry," Science, *57*, (1923), 483, the proteins are peptones held together relatively loosely by forces of primary valence. He assumes that the swelling of a protein jelly causes a dimunition in the forces holding the peptones together. J. A. Wilson points out that on this basis, the swollen protein or one in which the bonds between the peptones had been weakened through previous swelling would be attacked by hydrolyzing agents much more readily than the unswollen proteins. The glue manufacturer should exploit the beneficial action of the alkali in swelling the protein and solubilizing undesirable matters. He has, however, to remember that after five days there is a real beginning of topochemical hydrolysis which means the commencement of degradation of the collagen proper.

Kuntzel, Angew. Chemie, *50*, 307 (1937), states that as the liming period increases the isoelectric point of the collagen shifts to a more acid position. This is indicative of a deaminization or a change in the amino-acid content of the protein. As the liming period increases the basic amino acids are affected, decreasing in amount. The acids histidine and lysine are the most drastically affected. E. R. Theis and T. F. Jacoby, Amer. Leather Chem. Assoc., July, 1941, give the following results of an examination of 5 special hide powders:

Liming Period, Hrs.	*Arginine*	*% Basic Lysine*	*Amino Acids, Histidine*	*Molecular Ratio, Histidine: Lysine: Arginine*
24	7.75	3.64	0.43	1: 9:16
72	7.14	2.50	0.34	1: 8:19
120	7.14	2.50	0.34	1: 7:19
240	7.14	2.28	0.33	1:12:43
360	6.52	1.50	0.12	1:13:48

(In 1938 Highberger found that the molecular ratio of histidine: lysine: arginine of purified collagen (not limed) was 1: 15: 23.)

The glue manufacturer must take steps to see that liming is discontinued before collagen is appreciably degraded. This is best done by working to a time table worked out according to experience and controlling the liming process from the laboratory.

Some manufacturers mince the raw material prior to liming. This is advantageous if economically possible as by shredding the protein matter, uniformity of action is more certain.

Liming is generally carried out in wooden or concrete vats or pits, using a saturated solution of lime. Bogue recommends 10 per cent of lime on the weight of stock but this is considered somewhat excessive; 5 per cent should be sufficient for all practical needs. Fleck recommends 2 parts soda and 3 parts quicklime to 300 to 400 parts stock.

There is no definite time for liming; everything depends upon the condition of the stock. Green material requires a much longer period than limed, or partially-limed offal. The use of stale limes charged with organic matter is definitely bad and results in appreciable waste through rapid hydrolytic changes of valuable glue-making protein. The lime liquor should be reasonably fresh. Control tests are: total alkalinity determination; estimation of amino acids and determination of dissolved hide substance.

WASHING AND DELIMING

The objects of washing after liming may be summarized as follows:

1. Removal of alkalies and other soluble salts.
2. Removal of soluble degradation products.
3. Swelling of protein.

Stock should be washed in the one mill for 12 hours, using plenty of running cold water.

Treatment with weak acid is necessary to effect complete neutralization and removal of the alkalies used in liming and final swelling. Either hydrochloric or sulphurous acid is employed, the latter being preferable if steps are taken to remove objectionable sulphites from the stock. Maximum swelling of the protein matter occurs in a solution containing about 0.0025 gm. of hydrogen ion per litre. E. C. Porter, J. Soc. Leather Trades Chem., *5*, (1921), 259 and *6*, (1922), 83, observed that a point of minimum swelling of hide powder occurs at a pH value of 4.8 (slightly above the isoelectric point) and the maximum swelling at a pH of 2.4 in acid solution and about 12.3 in alkaline solution. Control of acidity is best done by means of simple spot tests with indicators, the action being stopped whilst the centre of the skin cut section shows slightly alkaline as tested by phenolphthalein.

GRADING AND ACIDULATION OF BONE STOCK

The bones are first sorted and all foreign bodies, particularly pieces of metal, removed. In most large yards electromagnets are available to facilitate the prompt removal of iron. Bones need crushing in special machines before they can be processed properly. Next follows the extraction of grease by boiling or solvents, using preferably petroleum distillate, B.P. 210° F. The degreased bones containing 50–60% calcium phosphate may need to be acidulated to ensure removal of inorganic matter. This is achieved by soaking the granulated stock in a weak solution of either hydrochloric or sulphurous acid.

$$Ca_3(PO_4)_2 + 4\,HCl = 2\,CaCl_2 + CaH_4(PO_4)_2$$
$$Ca_3(PO_4)_2 + 6\,HCl = 3\,CaCl_2 + 2\,H_3PO_4$$
$$Ca_3(PO_4)_2 + 4\,H_3PO_4 = 3\,CaH_4(PO_4)_2$$

Addition of lime precipitates acid phosphate:

$$CaH_4(PO_4)_2 + CaO = Ca_2H_2(PO_4)_2 + H_2O$$
$$2\,H_3PO_4 + 2\,CaO = Ca_2H_2(PO_4)_2 + 2\,H_2O$$

A period of several weeks is required for complete acidulation of the stock. This process is referred to again in the next chapter.

CHAPTER VI

EXTRACTION OF GELATINE FROM GLUE STOCK

EXTRACTION OR BOILING

THE term boiling as applied to the extraction of gelatine or conversion of the collagen into gelatine is a misnomer as the temperature does not exceed 90° C. and is usually within the range 70 to 80° C. The secret of success in extraction or cooking depends on the careful control of the conversion via hydrolysis of the anhydride of gelatine (collagen) into gelatine. If the heating is continued for too long a period then there is a lowering of the adhesive properties of the glue. Linder and Frost, Eng. News, 1915, *72,* 178, found that heating a glue solution for 20 hours at 65.5° C. effected a reduction in strength of from 30 to 45%. Members of the British Research Committee 1922–1932 are not in agreement with the above statement and their work would appear to indicate that the effect of prolonged heating of a gelatine solution at 60° C. and of glue solution at 80° C. is inappreciable. The author considers that there is a fall in adhesive properties when heating of the glue solution is extended beyond the necessary period and recent work by I. I. Sokolov, Colloid Journal, U.S.S.R. 1940, *6,* 815, is fairly conclusive proof that the changes which occur when gelatine is thermally denatured (boiled for 60 hrs. under reflux) adversely affect its main adhesive properties. Apart from chemical changes the resultant gel is more porous and the glue film less able to resist the shearing stresses.

There are two general methods of extraction or cooking: the open and the closed.

The open process of boiling is carried out in large pans, preferably made of aluminium, or in the case of the highest grade photographic gelatine, special vitreous enamelled containers. The heat is applied by means of an open fire, a steam jacket, coils, by forcing live steam into the liquid, or by a water jacket. An excellent means of heating is achieved by the use of the steam-jacketed pan, this method allowing of better regulation of temperature than any other. The use of steam coils enjoys a vogue in Great Britain but it entails a certain waste of energy by friction of the steam in the coil as well as considerable expenditure for initial outlay and liability of joints leaking. When live steam is used, the temperature is somewhat uncertain, and condensation occurs unless the steam is superheated. Water jackets were once the common means of extraction, but, owing to difficulty in maintaining one fixed temperature, they have fallen into disfavor.

As regards heating by an open fire, the disadvantages of this method are all too obvious, for overheating in certain parts of the boiler causes burning of the stock, while the impossibility of regulating the temperature causes loss by hydrolysis.

As regards the closed methods of extraction, these are carried out in autoclaves under a pressure of from 10 to 15 lbs. Bones, etc., are always extracted by this means, and for this material the closed method is eminently satisfactory. For hide and skin offal, boiling under pressure slows down extraction, as when water is squeezed out of the stock it is replaced only very slowly.

The following conditions are desirable as regards the boiling of hide and skin offal:

High concentration of glue liquor
Immediate removal of dissolved glue from zone of highest temperature
Minimum pressure
Production of a clear liquid

The stock is dumped into the boiler until the latter is almost full, then covered with hot water. Heat is applied and the temperature maintained at 140° F. for several hours or until the liquor has dissolved at least 6 to 7 per cent of its weight of glue. The liquor is drawn off through a valve in the bottom, and fresh water added. The heat is now maintained at 10° or 15° higher, and after about the same time, the liquor is drawn off as before. Four or five such "runs" are generally made, the last being at a temperature of about 210° F.

The greatest care must be taken to remove the "skin" which always forms on the top of the glue liquor. This film will cause the finished product to show up streaky and uneven in color if not removed at this stage. The usual practice is to ladle it off the surface, then add it to the next batch of stock for boiling.

In order to hasten the extraction, and speed of manufacture is an important consideration in this industry, some technologists agitate the liquor during boiling.

Probably the safest method of speeding-up production is to shred the glue stock, but, as pointed out earlier, this is rather an expensive procedure for small quantities, and needs careful costing before general adoption. The shredding should always be carried out on limed stock, or, better still, prior to liming.

The most popular method of boiling glue stock in Great Britain is the ordinary open-vat process, whereby the liquor is heated by means of live steam and agitation afforded by simple hand devices, such as small paddles, etc. This procedure, whilst suitable for the production of small amounts of glue and gelatine, is uneconomical and quite unsuitable when the process of manufacture is continuous and on a large scale.

NOTES ON THE EXTRACTION OF BONES

Bones are treated on somewhat different lines from those on which the other raw materials used in the manufacture of gelatine and glue are treated.

The object of the glue technologist is to achieve the following results:

1. Removal of dirt and blood, etc.
2. Removal of oleaginous matter.
3. Removal of calciferous and general mineral skeleton.
4. Extraction of remaining ossein.

The green bones on arrival are always crushed, making use of any of the standard machines, most of which have two pairs of heavy rollers with cutters, and a revolving screen for separating the particles into rough: ½ in. or ¼ in. and fine dust. The crushed material is then well washed in one of the washing machines described in an earlier chapter. Great stress must be laid upon this preliminary washing, as the presence of blood and extraneous matter will affect the purity of the bone fat to a very appreciable degree. Bogue advises treatment with dilute sulphurous acid, as this would keep the stock sweet and by its bleaching action ensure a good quality glue and fat.

J. C. Kernot and Miss N. E. Speer (Second Report, Adhesives Research Committee, 1926, 17–22) state that the maceration of bones in a dilute alkaline solution, previous to extraction, improves the quality of the glue. The author has attempted some experiments on the manufacture of glue from junk and other inferior quality bones, and he has found that by acting up to the suggestions of the Report a greater yield of glue is obtainable which is of better color.

There are two methods of degreasing:

1. The wet process, necessitating the use of water of 100° C. and at increased pressure.

2. The utilization of solvents, such as benzene, petroleum, etc.: dry process.

1. The crushed bones are placed in large autoclaves and boiled for a short period. By increasing the pressure, it is possible to cut down the period of treatment. The greatest care should be taken to ensure that the boiling is not prolonged to the stage of actual extraction of the gelatine. The bone substance is removed after degreasing and laid out on canvas bags to dry. The aqueous liquor containing the fat is run off into shallow vats, where it is allowed to cool and the grease skimmed off and refined. Bone fat from the above process is always of a better color, and generally superior to samples obtained from the dry or solvent method. It may be reckoned that 90 to 99 per cent of fat can be extracted by this means.

2. A far superior, though costlier, extraction process is the solvent one. Bogue says that by the use of benzol, carbon disulphide, or any of the well-known solvents, it is possible to remove about 99.90 per cent of fat.

The essential point to bear in mind, when considering this process, is that everything depends upon the percentage of moisture in the crushed bone, 10 per cent being reckoned as the maximum. Various patents have been taken out to protect the manufacture of special degreasing plants. The majority, however, are on the well-known Soxhlet principle, which permits of a continuous treatment of the material with hot spirit. The disadvantages of the method are:

1. The cost of the degreasing plant is rather excessive, and the expense of running appreciable, owing to the unavoidable loss of spirit during distillation.
2. A small percentage of gelatine is extracted, especially if the temperature is high. This results in the lowering of the gelatine yield and diminution in the value of the bone fat.
3. The bone fat is usually dark colored, and, consequently, of lower value than the lighter material obtained during the wet process.

The advantages of the method are:

1. Almost total, that is maximum, speed of extraction, which means that a uniform material is at hand for extraction of the ossein. Again, the method is reliable, and the percentage of fat in different samples of treated bones does not differ more than a decimal point or so.
2. Continuity of the process, allowing for maximum output.

There is no doubt that if large quantities of material are to be treated, the solvent method will prove more efficient and economical in the long run, but when the manufacture is intermittent and the batches are small, then the author advises the adoption of the wet process.

The degreased material is now ready for treatment with acids to dissolve out the calcium phosphates and other mineral salts. Glue manufacturers usually employ large shallow wooden vats or tubs to effect this decalcifying. About 10.5 per cent hydrochloric acid or 15 per cent sulphurous acid is usually found to be sufficient. Sulphurous acid is preferable and can be made very simply by passing sulphur dioxide gas into the water until the desired strength is reached.

The reaction which takes place is as follows:

$$Ca_3(PO_4)_2 + SO_2 + H_2O = Ca_2H_2(PO_4)_2 + CaSO_3$$

The skeleton of ossein remaining after treatment should be well washed in running water until neutral.

The extraction of gelatine from the crushed bones, which may be undecalcified or decalcified, is best undertaken in digesters at a steam pressure not exceeding 30 lbs. per sq. in. The British Adhesives Research Committee, Second Report, is of the opinion that before digestion the bones should be macerated in alkali to remove mucoid and albuminoid substances from ossein. Treatment with N/100 caustic soda followed by washing in running water will remove these undesirable proteins which lower the adhesive properties of the glue. The digesters used for extraction are steel cylinders with convex ends having a large manhole at the top for the addition of fresh bones and another at the bottom for discharging the spent material. Before extraction, steam is blown through the bones in order to clean them and to remove any traces of solvents. When the digester is filled with steam, the outlet is closed and pressure allowed to increase to the desired extent. When the pressure has been released, water preheated to 100° C. is run in to effect extraction. The following table compiled by the British Research Committee (Second Report, 1926) shows the differences in the physical properties of glues extracted at varying pressures.

Pressure per sq. in.	*Per Cent of Non-Protein Nitrogen*	*Jelly Strength (Comparative Figures)**	*Tensile Strength**
10 lb. 15 min.			
1st extraction	1.54	50– 90	1,205
2nd extraction	0.98	70– 90	....
10 lb. 30 min.			
1st extraction	1.12	70– 90	1,160
2nd extraction	1.80	30– 40	875–1,040

Pressure per sq. in.	*Per Cent of Non-Protein Nitrogen* (*Continued*)	*Jelly Strength (Comparative Figures)*	*Tensile Strength**
10 lb. 45 min.			
1st extraction	0.98	70– 90	1,140
2nd extraction	0.98	70– 90	1,140
10 lb. 60 min.			
1st extraction	0.98	70–110	1,203
2nd extraction	1.12	70–100	1,140
20 lb. 15 min.			
1st extraction	1.40	70–110	1,205
2nd extraction	0.84	70–130	....
20 lb. 30 min.			
1st extraction	0.98	90–130	1,245
2nd extraction	0.84	90–130	1,290
20 lb. 45 min.			
1st extraction	1.00	90–130	1,213
2nd extraction	1.05	70–110	1,200
30 lb. 15 min.			
1st extraction	...	70–120	1,185
2nd extraction	0.84	60–100	....
40 lb. 15 min.			
1st extraction	1.26	90–130	1,200
2nd extraction	1.26	50– 70	....
50 lb. 15 min.			
1st extraction	1.26	70–110	1,200
2nd extraction	1.26	30– 50	....

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* Non-protein nitrogen is that part of the nitrogen originally present in the glue that is not precipitated by addition of saturated acid solution of magnesium sulphate. A 10% jelly is used to determine jelly strength. Tensile strength according to British Standard specifications.

The best results are obtained at a pressure of 20 lbs. per sq. in. but it is claimed that for the first extraction a pressure of 25 lbs. per sq. in. is advisable and then to lower it by 5 lbs. per sq. in. for the final extraction.

The speed or rate of extraction of gelatine from bones is largely controlled by the rate of diffusion of gelatine and water through the pores of ossein. This means the preliminary treatment of the bones must be designed to achieve complete uniformity of porosity and particle size. The latter may be secured by ensuring that when crushed the bone particles will be able to pass through a sieve of the correct mesh. The importance of uniformity of particle size cannot be over-emphasized as it has direct influence on the rate of extraction. Porosity of a high degree is possible if degreasing has been thoroughly completed and the bone decalcified, washed and treated with a dilute alkali to remove mucoids and albuminoids, followed by further washing.

Employment of high pressures has the disadvantage of increasing the difficulties of filtration and clarification and for this reason, amongst others, it is advisable always to use the minimum pressure which can be relied upon to give the best yield.

After extraction, the bones are removed from the digesters or open kettles, etc., dried in a rotary drier and then ground up for sale as a fertilizer.

BONE FAT

Bone fat occurs commercially as a dark brown grease possessing an offensive odor, and containing large quantities of free fatty acids and lime soaps, the latter being formed by the action of fatty acids on the lime salts of the bones. It is used for coarse lubricants and soap, or bleached for candle-making. The manufacture of ordinary commercial bone fat can be discussed under two headings, "boiling out" and "solvent extraction" processes, each having its advantages and special characteristics, and an outline of the two methods will be given.

In the "boiling out" process, the fresh bones are first placed in a steam-jacketed pan and covered with boiling water, the mass being kept at 100° C. for 5 hrs. The mixture is then allowed to cool. While still fluid, the grease which rises to the surface of the liquor is removed and run into a lead-lined tank for refining. This is performed by means of aqua regia, 1.5 per cent on weight of fat being generally the quantity used. (Aqua regia is made by mixing one volume concentrated nitric acid with four volumes concentrated hydrochloric acid.)

The aqua regia should be well mixed with the fat by means of a wooden plunger or pole. After five or six hours, warm water is added and the acid liquor run off. The fat is then washed repeatedly with warm water until the last trace of acid is removed, and it is then ready for barrelling. When old bones are used, it will be noticed that during the slow cooling of the fat a greyish-white mass separates, upon which floats a brownish-yellow oil. The solid portion is used for soap manufacture, while the liquid oil is refined in the usual way.

Many solvents can be used for the second method. The most commonly used are the following: carbon disulphide, benzene, petroleum and chlorinated solvents. Lewkowitsch gives the following method: "Bones that are no longer fresh are usually extracted with benzene in digesters under pressure, or in open apparatus." The method in which pressure is employed is the more dangerous one, and has not infrequently led to explosions. The advantage which this method offers is that practically the total amount of fat contained in the bones can be extracted, the actual yield depending on the nature of the solvent and the time during which the solvent acts on the bones as also on the construction of the apparatus. That apparatus will be the best in which the volatile solvent is so successfully condensed that only a small amount of it is lost. The fat obtained by the extraction is dark brown, and has a very penetrating, unpleasant smell. Besides a considerable amount of free fatty acids, this fat contains lime soaps, calcium lactate, calcium butyrate, hydrocarbons from the petroleum and coloring substances. This kind of fat cannot be bleached successfully, and even if some immediate improvement is obtained by bleaching, the color, as also the unpleasant smell, will "revert a short time after bleaching. Whereas the bone fat obtained by the second process is utterly unsuitable for soap-making and can only be worked up in candle-making." Generally speaking dry stale bones are extracted by means of volatile solvents, while fresh ones are usually boiled and the grease recovered as explained (boiling-out process).

Some manufacturers remove the oleic acid from bone fat by means of milk of lime. The fat is stirred well in a solution of calcium hydroxide, when the oleic acid is precipitated as calcium oleate and almost wholly removed. The free oleic acid can be recovered by treating the precipitate with sulphuric acid, free oleic acid, and insoluble calcium sulphate being obtained.

EXTRACTION OF FISH WASTE

A high grade glue or gelatine may be made from fish skins, particularly the skins of cod, haddock, ling, flat fish, sharks, skate, rays, etc. If properly handled fish offal may also be utilized to make medium grade liquid glues. British Pat. 235,635, which is based on the work of the British Adhesives Committee, gives a method of working fish waste which is of great practical interest. The stock is first thoroughly washed in running cold water to remove all soluble mineral salts, especially common salt. After this the skins are macerated in very dilute alkali, the duration of the treatment varying according to the quality of gelatine desired. [Only very dilute alkali, 0.2% caustic soda or saturated lime solution, is used.] Skins of cod should be macerated with dilute alkali for a period of 24 hours, the alkali being changed at least three times during this period. In order to remove excess of alkali the skin is next subjected to thorough washing followed by maceration in very dilute acid, preferably sulphurous or hydrochloric acid (0.2%) for 24 hours. The offal must be again washed in running water for several hours and extracted in open kettles at 60° C. in place of 80 to 90° C.

GLUE FROM MIXED COD-HADDOCK AND CATFISH SKINS

Ratio Gelatin: Water	*Failing Loads in lbs.*	*Mean Failing Load in lbs.*
Regular dry test:		
1 : 1½	2,910; 2,975; 3,226	3,037
1 : 2	2,850; 2,980; 2,800	2,877
1 : 2½	2,825; 2,190; 2,100	2,375
1 : 3	2,350; 1,200; 1,055	1,535
Wet heat test:		
1 : 2½	1,760; 1,610; 2,200	1,856

The author is of the opinion that the open process of extraction is eminently suitable for marine offal, use being made of the steam coil, which should be at the bottom of the vat and covered over by means of a false lattice bottom. It frequently happens that if the fish offal is extracted under pressure, a product is obtained with a most objectionable odor, which, of course, lowers the quality of the glue. The question of odor is of supreme importance. The following points are worthy of special consideration in regard to the manufacture of fish glues:

1. Careful preliminary processing designed to remove all impurities and to solubilize protein matters unsuitable for glue making.
2. Quick extraction without pressure if possible.
3. Minimum number of runs.

It is claimed that a high grade gelatine can be made from fish skins provided the utmost care is taken in processing.

Bogue gives the following account of the extraction of fish waste:

> The fish skin and waste stock ordinarily are agitated in running water in large tanks for a period of 12 hrs. or so, or until a sample of the wash water on analysis shows a low percentage of chlorides. The stock is then thrown into false-bottomed tanks, called "cookers," which usually have a layer of excelsior on their false-bottoms. The stock is covered with water, and a slow stream of steam is passed into the tanks. The length of the cooking period varies with the nature of the glue stock, fish waste requiring longer cooking than fish skin stock. Usually, two runs are made; that is, the liquor formed by the cooking of the stock is drawn off when it becomes sufficiently concentrated, more water is added and the cooking is continued. The average concentration of the glue liquors is about 5 per cent. The first run of glue liquor is the better one.

GLUE FROM CHROME LEATHER WASTE

The extraction of glue from chrome leather waste has become of great importance in wartime and glue manufacturers are very willing to handle this troublesome material. Analysis of four samples of glazed kid is given below:

	1	*2*	*3*	*4*
Moisture	15.42	13.6	15.45	17.2
Fat and Sulphur	9.04	3.18	7.03	5.11
Sulphur	0.31	....	....	....
Chromium sol. in pet. ether	0.052	Nil	0.0178	Nil
Water solubles	1.50	1.29	1.10	2.42
Hide substance	61.32	65.21	57.0	62.86
Chromic oxide	3.49	3.66	3.38	4.18
Basicity	70.3	53.4	50.0	60.4

Before treating the chrome leather with the aim of removing the chrome and detanning, it is advisable to shred the leather, otherwise there is considerable difficulty in effecting penetration of process liquors. Trotman, in an early British patent dealing with the detanning of chrome leather, treated it with dilute acid or weak alkali such as lime water, then subjected it to an oxidizing agent capable of liberating hydrogen peroxide, such as sodium peroxide. The chromic oxide is converted into the alkali chromate, which can, of course, be recovered while the hide substance is in a fit condition for conversion into glue. M. C. Lamb (Brit. Pat. 132,864, 1920) utilized for detanning saturated dibasic acids such as tartaric, malonic and oxalic acids and also acids of the lactic acid series. The leather scrap is soaked in this acid solution until complete detanning occurs. The chrome is recovered and the glue stock utilized in the usual way.

Stripal (Brit. Pat. 3437/1910) detans chrome leather by treating the shredded material with 1–5 per cent solution of either hydrochloric or sulphuric acid at a temperature of 50–100° C.; the patentee claims that the leather is completely detanned. Another method is due to A. A. Bergin (Brit. Pat. 226,722/14–24). The leather scrap is boiled with water containing 1–2 per cent of "caustic burnt magnesite" calculated on the weight of the leather. 0.035 per cent of lime or other alkali can be added if desired. The leather is boiled repeatedly in the alkali solution and after each boiling the glue liquor is run off; this is continued until all the leather has been extracted.

J. Mayer Sohn (Brit. Pat. 235,548/1925) is responsible for an interesting method of detanning chrome leather. He subjects the finely-divided leather to the action of barium peroxide under pressure in an autoclave. The barium sulphates and chromate are separated from the glue liquor, which is then processed in the usual way. The barium chromate is treated with sodium sulphate and hydrochloric acid, and the barium recovered as barium sulphate.

By far the most efficient method of extracting the chrome from leather is by treating the leather with a solution of Rochelle or Seignette salt, the method being due to Wilson and Procter. The process relies upon the well-known fact that the salts of the hydroxy-acids, such as tartaric, form complex ions with chromium, and thus render its removal from chrome leather comparatively easy. Berestovoj and L. Masner (Jour. Soc. Leath. Chem., 1925, *9,* 449–453), in discussing the efficiency of chrome extracted by means of Rochelle salt, give some conditions which have to be fulfilled before satisfactory results can be obtained. The most important factors to take into consideration are temperature, surface of the leather, the amount of salt, and concentration of solution. They found that 1.5 gm. of sodium potassium tartrate per 1 gm. of leather gives the best results. The optimum temperature for the reaction was found to be from 60–80° C. and the extraction of the chrome to be independent of movement of the leather, but proportional to the time of extraction, temperature, presence of neutral salt, and the concentration of the solution.

The chromium compounds were found to be very difficult to recover from the solution, but the tartrate could easily be recovered with sulphuric acid. (This is contrary to Procter and Wilson; see Jour. Soc. Leath. Trades Chem., 1916, 156.)

Wollf, in a German patent, obtains chrome alum from the chromium recovered from waste chrome leather. The shredded material is treated with sulphuric acid at 80–90° C. until it has all dissolved, when excess of lime is added to precipitate the chrome together with all the sulphate present. The precipitate is dissolved in a definite quantity of sulphuric acid and potassium sulphate, and from this solution, after suitable classification and concentration, the chrome alum is crystallized out and used in the making up of one bath chrome liquors. It is necessary to add that the glue liquor is freed from any traces of lime by passing through it a current of carbon dioxide.

J. Landau and E. Trepka (Ger. Pat. 365,448/1921) treat the shredded leather with a fat-splitting agent, such as Twitchell reagent, contact oil, etc., in the presence of an alkali.

A very interesting method of detanning, in which enzymes are utilized, is due to Rohms' German Pat. No. 303,184. The leather is subjected to the action of dilute caustic soda, and the residue treated with enzymes of the pancreatic juices. Ammonium salts, amino acids, etc., are added with the enzymes, and are said to act as an "inhibiting" agent.

In reviewing the many methods of detanning chrome leather, the author considers that one or two are of outstanding merit and warrant practical trial. Wilson and Procter's method, embracing the use of Rochelle salt, is, without doubt, the most promising method. The processing salt can be recovered from the solution, which, of course, considerably cheapens the process and a very good quality glue stock obtained from the detanned stock. The method due to Lamb, when oxalic acid is used, is a very cheap one, the only drawback being that the glue liquor contains a small percentage of the free acid which, to some extent, lessens the tenacity of the glue.

Although other hydroxy acids are mentioned, such as tartaric, malonic, etc., these cannot be used on any practical scale on account of their excessive price. The method due to J. Mayer Sohn, using barium peroxide under pressure in an autoclave, is one which recommends itself on account of the speed of the reaction and efficiency, that is, when a large quantity of leather is to be treated.

TANKAGE, AFTER EXTRACTION OF GELATINE

Tankage from the extraction vessels can, after drying and grinding, be used as a fertilizer, either being sold as a simple nitrogenous manure or mixed with basic slag, phosphates, lime, etc., to make compound fertilizers.

In the drying of the material the best method is to spread it out on wire netting and expose it to a safe temperature in a sealed stove. It is always advisable to keep turning the tankage during drying, otherwise it may overheat and burst into flames.

When there is a large percentage of wool and hair in the waste matter, the fertilizer value of the product is considerably diminished. In normal times it is not a commercial proposition to sell the washed and dried hair and wool to textile manufacturers or plasterers; there is practically no real market for such inferior and almost worthless material.

CHAPTER VII

FILTRATION, CLARIFICATION AND ADDITION OF CHEMICALS

AFTER extraction, the gelatine liquor is run into large shallow vats for settling. A temperature of 60° C. is maintained, the grease rises and is skimmed off and the flocculent impurities settle. Common impurities in the liquor are undissolved organic matter, lime soaps, grease and hair, as well as mineral and bone particles. The suspended material can be removed by filtration, but it is recommended that prior to this all the larger particles should be removed by screening the glue liquor through wire cloths. The best results in filtration are achieved by utilizing a filter aid such as diatomaceous silica, paper pulp, carbon, etc., which is able to effect considerable clarification of the liquor. It is important, however, to use a high grade of filter aid free from objectionable impurities such as soluble salts, organic matter, coloring materials, taste or odor imparting bodies, gritty particles. Another qualification which is always specified in connection with the use of filter aids for all foodstuffs is that they must be completely inert or unreactive in the material being filtered. The physical properties of the aid should be such that it is well adapted to form an open interlocked structure with extremely fine pores and with a strong tendency to stick or jar in small channels. Once these channels are partly blocked by the larger particles, the smaller ones are soon arrested and an extremely fine filtering surface results. J. A. Pickard, Industrial Chemist, May 1928, states that:

1. With precipitates of hard, non-deformable particles formed on well defined filtering surfaces the rate of filtration is directly proportional to the pressure and inversely to the cake thickness, and the formula $R = \frac{KAP^*}{L\mu}$ applies with fair accuracy.

L = thickness of cake
K = constant for the material
A = area of filter surface
R = rate of flow
P = pressure
μ = viscosity of liquid passing through.

2. With precipitates of soft, deformable particles, the rate of filtration is not increased proportionately with increase of pressure, and may even be diminished.
3. Cakes of hard non-deformable particles are uniform throughout, and their character is unaffected by pressure of filtration or concentration of solid in the previous filtrate.
4. Cakes of soft, deformable particles will be drier and more compact at the filter surfaces than at the outer surface, and will be the more compact the higher the filtration pressure.

The substances in suspension in the gelatine liquor are extremely difficult to eliminate completely on account of their sticky and colloidal nature. The manufacturer is not dealing with hard and non-deformable spheres, but colloidal particles carrying practically the same electrical charge as the gelatine particles themselves.

Bogue recommends the use of the best cotton cellulose and a filter which allows for a loose packing of the pulp.

The greatest care should be taken in the working of the presses. If they are not well washed after use there is a

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*** It should be explained that this formula of Poisenille forms the basis of the mathematics of flow liquids and filtration in general.**

danger of moulds forming and these, if allowed to infect the gelatine, result in a lowering of the quality of the finished product.

Rideal, "Glue and Gelatine," stresses the above point. "A press, particularly a wooden one, should always be kept scrupulously clean; if it is absolutely necessary for the wood to remain at rest for a time, it must be washed with dilute chlorine water, or very weak chloride of lime, then with clean water, and allowed to dry, but it is rare for a leak not to occur on resuming work."

Gunmetal presses are preferable to wooden or iron ones as they are easier to keep clean and give a clearer and finer filtrate. There are, of course, a number of excellent filter presses on the market, e.g. Kelly or Sweetland, Oliver, American Continuous Filter, etc., but although the plate and frame press is the oldest and in many ways uneconomical, particularly as regards operating costs, it has been found well adapted for glue and gelatine manufacture. Use of centrifugal machines for the separation of suspended particles prior to filtering is recommended for high grade glues and gelatines.

DECOLORATION AND CLARIFICATION

If the gelatine is of exceptionally good quality sometimes filtration is sufficient, but generally the solution needs clarifying in order to produce the brightest and clearest product. Amongst the common clarifiers are alum, followed by a small quantity of milk of lime, calcium sulphate, albumen, blood and oxalic acid. The oldest material used for the clarification of high grade gelatine is egg albumen.

A well-known method of clarifying glues by means of aluminium sulphate is as follows: The glue liquor is run into vats provided with a steam column or coil and some means of agitation. Crude sulphate of alumina is added and the mixture is agitated, then heated to about 80 to 90° C., until the coagulation is complete. The steam is then turned off, the liquor is allowed to cool and the flocculent precipitate to settle, which takes about 5 or 6 hours. When albumen is employed the temperature of the gelatine liquor should be about 50° C. before the former is added. The temperature may then be increased until 94.3° F. is reached when complete coagulation takes place. Generally the period needed for absolute settlement is 30 hours.

Of considerable interest is the method of decoloration and clarification described in B.P. 500,857.

The gelatine in a neutral solution at a temperature of 55 to 75° C. is treated with hydrated aluminium oxide which is later separated and removed from the liquor by centrifugal action, filtration, etc. It is stated that the concentration of the gelatine or glue solution may be kept between 3% and 11%. The operating conditions are designed so that the separation of the hydrated aluminium oxide, which has accomplished its decolorizing action, may be satisfactorily effected by decantation or by a mechanical process, such as centrifuging, leaving a product which is easily filtered, even at relatively high concentrations. Cream or paste of hydrated aluminium is introduced in general in an amount of from 5 to 15% calculated as dry $Al(OH)_3$ of the weight of the air dried gelatine or glue contained in the solution. After introduction of the aluminium hydroxide, the liquor is kept at 55 to 75° C. and the whole is agitated from time to time in such a way as to keep the hydroxide in suspension (about 60 minutes). The solution is then centrifuged and filtered.

REDUCING ASH CONTENT OF PHOTOGRAPHIC GELATINE

The normal ash content of high quality gelatine is 2–4% and for photographic applications it is very desirable that the ash content should be reduced to 0.2% or less. The purification of gelatine is a difficult matter, but during recent years considerable progress has been made. Of theoretical interest is the purification of gelatine by electrolysis after thorough washing with N/1000 HCl and water to remove the bulk of the salts. In the experiments carried out by the Adhesives Research Committee, a 20% gel was subjected to the action of an electric current without the use of a membrane. The jelly was simply cast in the bottom of a bell jar which was then placed in a trough containing water and mercury (negative pole). Water was then placed on the top of the jelly in the bell jar and platinum wire inserted into the layer of water at the positive pole. After being subjected to the current (PD = 200 volts) for several days, the jelly was removed and examined. Ash content of the gelatine which before the passage was 0.25% reduced to 0.02% or less.

Of considerable interest is a recent patent (Brit. Pat. 521,646) taken out by Dr. E. E. Jelley of the Canadian Kodak Co. This patent covers a process whereby the gelatine solution is freed from calcium salts and saline matter by passing through various filters. The decrease in the calcium content has the effect that for example dyes which normally would be precipitated or partly precipitated in the form of calcium salts when added to the gelatine solutions, or to the photographic silver halide emulsions, can now be added without any harm or variation in their physical properties. The process, which depends on the filtration of the aqueous gelatine solution through zeolite filters, does not interfere with the pH of the gelatine, whereas washing with acid saline solution, which is the usual method of purification, does interfere with this. The concentration of the gelatine solution before filtering should be 10–20% and must be warm, 100° F. If this gelatine is contaminated with saline matter, e.g. chlorides, sulphates, etc., the aqueous solution should be passed through an acid-absorbing filter composed of a synthetic resin (B.P. 450,309 and B.P. 506,291). These two patents cover the production of resins obtained from aniline, meta-toluidine, sym-m-xylidine, m-phenylene-diamine. Experiments carried out by the inventors, Adams and Holmes at the Chemical Research Laboratory, Teddington, England, show that these resins possess very great absorptive ability insofar as the amines of the solutions are concerned.

When acid solutions (0.0035 N) were passed through 10 grams of reactive resin and washed free of excess base, the volumes from which the acid was completely removed are given in the table.

Resin Obtained from:	HCl	HNO_3	H_2SO_4
Aniline	1,100	1,000	1,200 cc.
m-toluidine	2,500	1,500	2,000 cc.
Sym-m-xylidine	1,800	1,800	2,300 cc.
m-phenylene diamine	2,600	1,800	2,300 cc.

0.0035 N solution of sulphuric acid and sodium sulphate were passed through the following resins.

Vols. of solution from which the SO_4 radical was completely removed:

	H_2SO_4	Na_2SO_4
Aniline	> 600	1,800
m-toluidine	> 700	2,200
Sym-m-xylidine	> 800	2,100
m-phenylene diamine	> 900	1,000

Bleaching of glues is undesirable but some manufacturers find it necessary in the case of very dark products. Sulphur dioxide, sodium hydrosulphite, basic zinc salts or formaldehyde, etc., are all recommended from time to time and claims are made for each one. Considerable lightening of the color may be produced by the use of sodium hydrosulphite but there is a loss in adhesive properties.

CHEMICAL ADDITIVES

To endow the finished glue or gelatine with special properties, various chemicals may be added to the liquor before or after evaporation. These additives are claimed to increase the flexibility of the glue film and render it more suitable for special applications; increase the rate of hardening or setting; increase the strength of the joint or improve the resistance of the film to water. Whilst there is no doubt that certain changes in the physical properties of the gel may be brought about by the addition of various chemicals, the scientific evidence available indicates that most additives cause a decrease in the jelly strength and tensile strength of the modified product. Experiments carried out by the British Adhesives Research Committee show that potassium dichromate is the only addition able to increase the strength of glue; formaldehyde has no effect on the tensile strength and sodium formate, sodium salicylate and glucose weakened the glue film considerably.

The table given below shows the results obtained.

Chemical	*Glue & Gelatine*	*Width, in.*	*Thickness, in.*	*Breaking Load, lb.*	*Tensile Strength, lb. per sq. in.*
Potassium dichromate	Gelatine	0.50	5.1	36.0	14,100
Potash alum, 3%	Gelatine	0.50	7.3	39.3	10,800
Sodium formate	Glue	0.50	10.7	40.8	7,600
Sodium salicylate	Glue	0.50	6.7	24.3	7,300
Glucose	Glue	0.50	8.1	12.0	3,000

Chemicals recommended for special purposes are given in recent patents. U. S. Pat. 2,103,776, 1937, describes a product which comprises an aqueous solution of an animal glue with the addition of small quantities of urea. U. S. Pat. 2,235,202, 1937, includes the use of a vegetable tannin and an alkali metal silicate. U. S. Pat. 2,246,405, 1939, also deals with glue solutions containing tanning agents, i.e. salts of aluminium and chromium. The product is claimed to be water resistant. Special chemicals are added to photographic gelatine to prevent fog and for other special purposes. Brit. Pat. 504,378, taken out by Kodak, Ltd., details some of the additives, i.e. non-chlorinated homocyclic benzene derivatives containing at least one nuclear hydroxy group, preferably dihydroxy benzene derivatives. These are added to an aqueous solution of gelatine together with an aldehyde, e.g. formaldehyde, acetaldehyde, glycolaldehyde, aldol or the straight chain compounds such as arabinose.

The use of antiseptics is not recommended as the presence of phenol, etc., have deleterious effect on the adhesive properties of glue and are objectionable if present in gelatine destined for photographic purposes. A number of preservatives have been recommended for use with edible gelatines. Thymol, chlorobutanol, sodium salicylate, parachlorometaxylenol, oxyquinoline sulphate, ethyl hydroxybenzoate, propyl hydroxybenzoate, butyl hydroxybenzoate, etc., in concentrations of 0.1–0.5% are suggested by L. Gershenfeld and D. Perstein (J. Amer. Pharm., 1939, *3*, *277–287*) for acid type gelatines; the following for basic treated gelatines: thymol, chlorothymol, chlorobutanol, parachlorometaxylenol, etc., in concentrations of 0.1–0.8%.

CHAPTER VIII

EVAPORATION

THE old forms of evaporators, such as the direct-heated metal vessel, steel jacketed pan, and open vessel provided with steam coil, are now things of the past, as they have proved both inefficient and uneconomical. Vacuum pans and Multiple Effect Film Evaporators are now regarded as the best means of carrying out this difficult operation, although the former suffer from certain disadvantages in practice. Multiple Effect Evaporators are now widely used in the glue and gelatine industry.

J. Arthur Reavell, in a paper on "Evaporation in the Chemical Industry with Particular Reference to the Kestner Evaporator," read at a meeting of the Society of Chemical Industry (Manchester Section), 11th April, 1918, gave the following description of the "Film" Evaporator:

> Paul Kestner, in the course of a long experience in all types of evaporators, particularly studied the horizontal film evaporator, and found out its great limitations. He therefore set himself to discover, if possible, a means of producing a perfect film (account follows of the evaporator). The tubes are 23 ft. long. The liquor is fed into tubes from a tank about 3 ft. above the bottom tube plate, and assuming that this liquor is hot, on steam being applied to the outer surface of the tubes, ebullition at once commences inside, releasing a large volume of vapour which must find its way to a region of lower pressure by passing

up the tubes. As a result, we have the phenomenon of the "climbing film". The liquor and vapour, on leaving the top of the tubes, meet a fixed centrifugal baffle, where the liquor is separated from the vapour, the liquor passing to the concentrated liquor tank, and the vapour to atmosphere or the condenser. The velocity of the liquor itself is thus used by means of centrifugal action to separate the vapours from the liquid.

In endeavouring to evaporate a liquid, one of the great objects is to transfer the maximum number of heat units per unit area from the heating medium to the liquor to be evaporated. Based on deductions from actual apparatus, and bearing in mind the results of theoretical and experimental research, the quantity of liquid evaporated in a tubular apparatus heated by steam would appear to vary with the following factors:

1. Area of heating surface; 2. temperature drop "temperature head"; 3. velocity of the liquid relative to the heating surface; 4. velocity of the heating steam; 5. specific volume of the heating steam; 6. viscosity of the liquid.

In practice, of course, the transfer is far from being the heat conductivity obtained through the ideal cubic centimetre of pure metal.

EVAPORATION

The gelatine is now ready for evaporation. This process is of very great importance, and cannot be dismissed in a few words. More attention has been paid by chemical engineers to the construction of evaporating vessels, than to any other plant used in the chemical industry.

The conditions under which heat is supplied to the metal are very different whilst the transfer takes place through a combined wall of water, oxide, metal, and incrustation.

The table of relative heat conductivities of the various components of the evaporators, including incrustation, water and air is illustrative.

Relative Heat Conductivity

	Gm. calories per cm.^{2}, thickness 1 cm., 1° C. drop per second	*Comparative figures. Copper 1000*
Copper	0.9	1000.0
Iron	0.167	186.0
CaCO	0.005	5.56
Silica	0.0025	2.78
Water (not in motion)	0.0014	1.56
Air	0.000056	0.062

	Kg. calories per m.^{2}, thickness 1 mm., 1° C. drop per hour
Copper	323,000
Iron	60,000
CaCO	1,870
Silica	935
Water	520
Air	21

	Theor. kgs. steam condensed per m.^{2}, thickness 1 mm., 1° C. drop per hour	*If the thickness is increased to 2 mm.*
Copper	605.0	302.5
Iron	112.0	56.0
CaCO	3.5	1.75
Silica	1.75	0.87
Water	0.98	0.49
Air	0.04	0.02

In referring to this table, Basil Heastie, in a paper on "Heat Transmission in Coolers, Heaters, and Condensers," read at a meeting of the Chemical Engineering Group, March 9th, 1923, gives the following interesting notes referring to the table:

From this it will be seen that a film of water 0.003 in. thick is equivalent in resisting heat flow to a copper wall 2¼ in., or assuming that the average tube wall thickness is 0.08 in., the resistance of the metal is 1/278th of that of the film. If steel be employed in place of copper, the resistance is increased by about 1/47th; whilst if a lead tube is used, the resistance is increased to 1/28th; and since for mechanical reasons it would be necessary to increase the tube thickness where lead pipes are used, the resistance would be greater.

The next factor is heat drop. In an open coil pan the transmission of the heat depends (other things being equal) upon the heat drop, or temperature difference. That is to say, if the steam in the heating coils is at 10 lb. pressure, the temperature of the steam is at 115.5° C., and assuming there is water in the vessel, the boiling point of which is 100° C., there will be a heat drop of 15.5° C.

When a vacuum is applied, the object is to increase this temperature drop. Taking the same figures as above, but with a closed instead of an open pan, the application of a 24 in. vacuum causes the temperature of the steam evolved from the liquor to be 60° C. instead of 100° C., so that the temperature drop is increased from 15.5 to 55.5° C.

Now as the rate of evaporation varies directly as the difference in temperature, a material advantage is gained by this increased temperature. However, while the rate of evaporation is proportional to the difference in temperature, there may be other factors which militate against this. That other factors do occur is evident, because, by increasing the steam pressure, the evaporation does not always increase proportionately.

In a "film" evaporator high temperatures can be used with advantage, because the surface is so disposed that the diameter is very small, even for great surface areas, whereas, in a bulk evaporator, such as a vacuum pan, a large surface area of tubes means a large diameter. Moreover, if high temperature, and consequently, high pressure is employed in this type of pan, many liquors which are sensitive to heat are destroyed, because they are too long in contact with the heating surface. In the "film" type evaporator which works continuously, the liquor is in contact with the heat for a few seconds only, and no "stewing action" takes place. Heat transfer also depends upon (a) the velocity of the liquor and vapor in relation to the heating surface, and (b) the velocity of the steam in relation to the heating surface. Speaking broadly, it may be said that the heat transmission varies directly as the square root of the velocity, so that if either velocity is quadrupled, the co-efficient of heat transmission is doubled. This is commonly spoken of as the effect of "circulation."

Considering now the principle of multiple effect evaporation, Reavell points out:

> All that happens in multiple evaporation is that, by alternate evaporation and condensation, the latent heat is exchanged successively, as a means of separating water from solids. Thus, neglecting losses and evaporation, etc., if 1 kilo of steam be condensed in the first calandria of a triple effect through which liquor is passing, 1 kilo of condensed water would be produced from the liquor in each of the calandrias of Nos. 2 and 3, and 1 kilo of vapour would be produced in number 3. If, therefore, we had commenced with 1 kilo of boiler steam and 3 kilos of water to be evaporated, we should have 3 kilos of condensed water and 1 kilo of steam at a lower temperature and pressure than that of the live steam supplied to the first effect. The cycle of operations finishes by producing 3 kilos of condensed water and 1 kilo of vapour at a low temperature and pressure—thus showing that what has happened is merely a transfer of heat.

The triple effect is a most convenient form of apparatus for normal works conditions, as it gives a high economy in working, with a moderate capital cost, and, unless the quantities of water to be evaporated are relatively large, it is seldom advisable to go beyond this.

Kestner & Co., Ltd., mention:

> A triple effect evaporator is usually operated with the last effect under vacuum, except in very special circumstances, the object being to get a high average temperature drop without excessive pressure in the first effect. In cases where the liquor to be evaporated is very viscous when cold, we run counter-current, so that the weak liquid enters the third effect and leaves either from the first when full counter-current is adopted, or from the second when working semi-counter-current. The steam passes from the first to the third effect as usual. The Kestner Evaporator is particularly well adapted for the counter-current working.

For bone glues, where the quantities dealt with are large, a double effect evaporator working under atmospheric pressure is usually employed, and this may be followed by a single effect finisher evaporator when high concentrations are desired.

For gelatine and high-grade glues the plant usually consists of a double or triple effect evaporator working under vacuum. For both bone glue and gelatine, where the quantities are small, it is sometimes economical to install simple effect evaporators of the climbing and falling type.

It should be remembered that Multiple Effect Evaporators permit of rapid working at comparatively low cost. The circulation is very rapid, so that the rate of evaporation is unusually high, and the liquor passes through in the shortest time. This is of the greatest importance when dealing with unstable substances, such as gelatine, etc., where hydrolysis may possibly take place and the liquor deteriorate.

Bogue mentions that "if dry glue in thin sheets is to be produced, evaporation may be omitted or carried to a glue concentration of only 5 per cent." In order to chill and work such a jelly, it must necessarily be of the finest quality. For the lower grades the concentration may be pushed as high as 50 per cent.

When the glue liquor has been sufficiently concentrated and allowed to cool, special care should be taken to prevent growth of micro-organisms. Air supply should be watched and the glue prevented from coming in contact with dirty surfaces.

The use of copper vessels sometimes means that traces of copper creep into the products. C. G. King and G. Etzel (Ind. & Eng. Chem., 1927, *19,* 1004–1005) found that down to 5–10 mg. of copper per day may produce toxic results. They also found that the presence of this metal accelerated the destruction of vitamin C. Experiments were made on the extraction of the metal by milk boiled in copper vessels, with the result that the pasteurization in copper apparatus added 0.1 part per million.

The presence of excessive proportions of copper in food products depends largely upon the acidity of the product. Gelatine containing excessive amounts of volatile or mineral acids would be very liable to dissolve appreciable quantities of copper.

COOLING

This is one of the most hazardous processes from the manufacturer's point of view owing to the liability of the gelatine being ruined by liquefying bacteria, such as bacillus subtilis, which is frequently present in the air and the spores of which are not destroyed even at a temperature of 120° C. There is also a danger of the gelatine being contaminated with metallic impurities and dust, or it might absorb certain noxious fumes or gases.

Purity can be ensured by the following means:

1. Use of monel metal or enameled plant.

2. Use of conditioned air with a very low bacterial count.

An alternative to (2) is afforded by the use of properly circulated air and the careful regulation of temperature and humidity, but naturally this is by no means fool proof. Formerly the method of cooling and drying used consisted of running the glue or gelatine liquor into metal cooling pans made of stout sheet zinc or heavily galvanized iron or aluminium. The temperature of 33 to 34° F. was maintained by means of a refrigerating plant. When the jelly was cooled sufficiently it was removed from the pans or vessels by cutting, immersing in hot water for a short time, or exposing to steam, the pan being returned for refilling. The cakes of jelly were then cut into thin sheets, either by machine or hand, and these were laid out to dry on fibre or zinc netting in a drying loft; temperature not exceeding 21° F.

Although in Great Britain there are still several quite large factories where the above method is carried out, it is no longer regarded as economical owing to the time lag between evaporation and drying. The longer the interval the greater the danger of contamination and consequent lowering of quality. Naturally, this is not so important in the case of glue, but for photographic and edible gelatine it is essential that great care should be taken to ensure the highest standard of purity.

A common practice is to flow the gelatine or glue solution from the extractor on to an endless rubber (preferably synthetic rubber) belt, 2½ ft. to 3 ft. wide and provided with ridges on either side to retain the liquid, and to blow on to the moving liquid surface cold, filtered air (15° F.). The speed of the belt is such that about 15 min. is taken up in passing through the cooling chamber in which is circulated air from refrigerating coils. The solidified gelatine is peeled off the belts, cut longitudinally by discs into ribbons 4 inches wide which are then delivered on to frames passing through the tunnel dryer. In one large plant in the United States this is 100 ft. long and has a cross section of 15 × 7 ft. The entrance air from the heating coils is from 95 to 100° F., depending on the humidity, and about 12 hours are required to reduce moisture content to the requisite degree. The thin, brittle ribbons of gelatine from the tunnel are crushed and ground, then graded to the desired mesh by passing over a vibrating screen.

Of considerable importance is the fact that the ground gelatine or glue is stored in bins, each bin being clearly marked with particulars of the batch, and representative samples are sent for testing: jelly strength and viscosity being the most important tests. Once the data from the laboratory are available, the manufacturer can blend the lots to obtain a standardized product possessing the desired properties. This mixing or blending is very important because it enables the manufacturer to guarantee a reliable product. In case of photographic gelatines blending is not desirable and for photographic emulsions a straight "one-source" gelatine is required.

If gelatine is cooled in open lofts the presence of ozone in the air (present in thundery weather) is liable to cause serious trouble as the jelly absorbs this gas very rapidly, being decomposed by it into oxidized products possessing no useful adhesive or "gelling" properties.

FOAM GELATINE

A fairly recent patent, U. S. Pat. 2,000,042, taken out in 1935 by S. E. Shepperd and J. H. Hudson, Eastman Kodak, Inc., describes a most interesting new method of finishing gelatine in the form of a foam. This possesses the practical advantage of absorbing and dissolving in water with maximum rapidity. The foam is produced by passing the liquor with an air lift through a baffle-type emulsifying apparatus.

The foam is then passed onto a chill roll or belt which is passing over a chilled surface, so that the foam structure is set. Gelling or setting is extremely rapid and it has even been possible to flow the foam onto a cold water surface which set and conveyed the foam. In any case, the set sheet of foam is taken from the first conveyor into air-drying sections, either in batch or on continuous driers. The time for drying is much reduced. The dried crepe or foam is then taken either continuously or in short sections and compressed. This is done by passing the band, sections or sheets of dried crepe between squeeze rolls at 500 to 1,000 lbs. pressure per sq. in. Foams and pressed foam gelatine have been prepared from sols. 3 to 20%. It is, of course, obvious that it is a great advantage to be able to work with such low concentrations as it eliminates costly evaporation and thus reduces manufacturing costs.

The following table shows the striking differences in dissolving foam and flake gelatines:

	TIME OF SOLUTION AT 40° C.		TIME OF SOLUTION AT 65° C.	
Gelatine, %	*Pressed foam, min.*	*Flaked sheet, min.*	*Pressed foam, min.*	*Flaked sheet, min.*
1	10	60	2	10
5	15	75	3	20
10	15	90	4	20
35	15	120	5	30

CHAPTER IX

RECOVERY AND PURIFICATION OF BONE FAT AND SKIN GREASES

IT HAS become of the greatest importance that all by-products and waste products should be fully exploited. The animal fats recovered from bones and hide and skin offal are valuable materials which, apart from their intrinsic value, cannot be replaced by imports. It is, therefore, incumbent on the glue manufacturer to plan an efficient recovery of these essential by-products and also to take the most energetic and intelligent means possible to increase their usefulness by carrying out their purification.

There are three main types of grease recovered by the glue manufacturer:

1. Bone fat.
2. Skin greases.
3. Tankage greases.

BONE FAT

Dealing first with bone fat, it should be clearly stated at the outset, that whereas in normal times this animal grease was always considered to be a low grade material suitable only for certain types of lubricants and for cheap soaps, today bone fat has become a valuable material greatly in demand by soap and grease manufacturers.

Lemkowitsch and Warburton (Chemical Technology of

Fats, Oils and Waxes, page 756) state that fresh bones from heads, ribs, shoulder blades, etc., contain from 12–13% fat. There is an appreciable diminution in the quantity of fat present in old bones due to the interaction of the fatty acids with the lime salts with the formation of calcium salts, e.g. calcium stearate, oleate and palmitate. Coincident with this drop in the percentage of fat present in old bones, there is also a steady deterioration in the quality of the fat. This is immediately evident by the dark color and unpleasant smell of the extracted fat. The obvious lowering of quality due to the exaggerated time the fat is in contact with the calciferous substance of the bone is due mainly to the following factors:

1. Hydrolysis of the glycerides with the formation of free fatty acids and glycerin.
2. Action of fatty acids on calcium salts and the solution of the calcium soaps in the grease.
3. Oxidation of the bone grease.
4. Presence in the grease of appreciable quantities of calcium lactate and smaller amounts of calcium butyrate as well as free butyric acid.

It will thus be obvious that bones should not be allowed to accumulate and lie around for weeks before processing. The fresher the bones, the higher the yield of fat and glue and the better is their quality.

Another factor influencing quality of bone grease is the presence of blood, excreta and dirt on the bones at the time of extraction. Bones should always be well washed with warm water before crushing and boiling. A good suggestion is to shovel the bones onto an iron grill or grating and then allow a spray of warm water, temperature 150° F., to pass over them for half an hour. Some glue manufacturers subject the washed bones to the action of sulphurous acid, 1½% solution, for two hours so as to bleach the bone and act as a preservative. This acid steeping bath is recommended as its use undoubtedly brings about a marked improvement in the quality of fat and glue. Great stress is laid on these preliminary cleansing processes as they ensure an improvement in the quality of the fat extracted. If desired, washing can be carried out when the bones are crushed, but this may mean a loss of ossein and fat and the writer prefers the method described above.

There are two standard methods of fat extraction:

a. Steam extraction.

b. Solvent extraction.

The usual procedure, and still the best, is to extract the fat from the crushed bones in specially designed iron digesters at a pressure of 55–60 lbs. per sq. in. The fat obtained in this way is run off with condensed water and allowed to settle. It is boiled up in coppers until the moisture is down to the required level, strained and, if necessary, filtered. A fat extracted from fresh bones is white to cream in color, of greasy consistency, not smeary or granular and possessing a faint but not unpleasant odor. Its specific gravity at 15.5° C. is 0.914–0.916; solidifying point 15–17° C.; melting point 21–22° C.; saponification value 190.9 mgms. KoH; iodine value 46.3–49.6.

The steam or autoclave method of extraction will secure a yield of 75% of the fat present in the bones and ensure minimum discoloration. To recover the remaining quantity of grease, solvent extraction using trichlorethylene or benzene is necessary. This method, which depends for its efficiency on the extraction by means of hot solvent vapors, produces a dark (yellowish to brown) grease possessing a characteristic unpleasant odor and often having a somewhat crummy consistency. Bone fat extracted with trichlorethylene usually contains 86–88% fat, 3–4% mineral matter and 4–5% water.

In the case of very old bones solvent extraction alone should be carried out so as to secure the minimum yield of fat. It is waste of effort to attempt the extraction of the fat by means of the autoclave method.

PURIFICATION OF BONE FAT

The plant required for efficient and economic purification, i.e. removal of impurities, bleaching and deodorization, need only be very simple. All that is required is a lead-lined tank for the acid treatment of the fat, an iron copper with a mixing device and equipped with steam coil or steam jacketed heating and a plate and frame type filter press fitted with steam heated plates.

Best quality, i.e. white bone greases, should be melted down in the iron copper tank and the occluded water allowed to separate out. The dry grease can then be heated up with 7% bleaching earth for 20 minutes and the mixture passed through the filter press.

In the case of low grade, i.e. dark bone greases, the method recommended is chemical bleaching with combined oxygen, employing in this case potassium or sodium dichromate and acid. For every 100 Kg. of oil, 0.5 to 3 Kg. of dichromate (usually 0.5–1.5 Kg.) is dissolved in 3–4 times its weight of hot water. Sufficient acid is used to give a slight excess over the theoretical. If hydrochloric is employed, it should be 18–20° Bé. (28–32%) and it can be mixed with the aqueous dichromate solution. The writer recommends 1¼–1½ Kg. of dichromate dissolved in four times its weight of water and 2½–2¾ Kg. of hydrochloric acid (commercial). The method is quite simple. The oil is warmed to 6–7° above its melting point and the dichromate solution mixed in with a stirrer, either with or followed by the acid. The mixture is then stirred until it resembles an emulsion, the mixing being facilitated if the acid and the dichromate solution are previously mixed before they are added to the fat.

The temperature rises 8–10° C. The process may require 1 hour or more. The mixture is allowed to stand, the chromic chloride solution drawn off and the oil washed with acidified hot water, then with pure water, until free from acid and chromic salts.

In some cases it is advisable to carry out a preliminary chemical bleaching with 1–1.5% of 60° Bé. sulphuric acid. Treatment should take place in the cold or in the melted fat, stirring constantly during the addition of the acid which must be poured in the lead-lined tank in the form of a thin stream. After half an hour's agitation a sample of the oil is removed and examined to see whether the carbonized particles have clumped together and left the oil clear. The material is allowed to stand for a few hours or overnight and the oil syphoned off the next day from the precipitated dark gummy mass. It is washed several times with 5% fresh hot water 80° C. until the wash water is neutral.

The general principles of grease purification may be considered under the following main headings:

1. Removal of coarse suspended matter by settling and straining.
2. Physical purification by treatment with bleaching earths and subsequent filtration.
3. Chemical bleaching with sulphuric acid or dichromate and acid.
4. Drying by further dry heating where it is necessary to reduce moisture content.

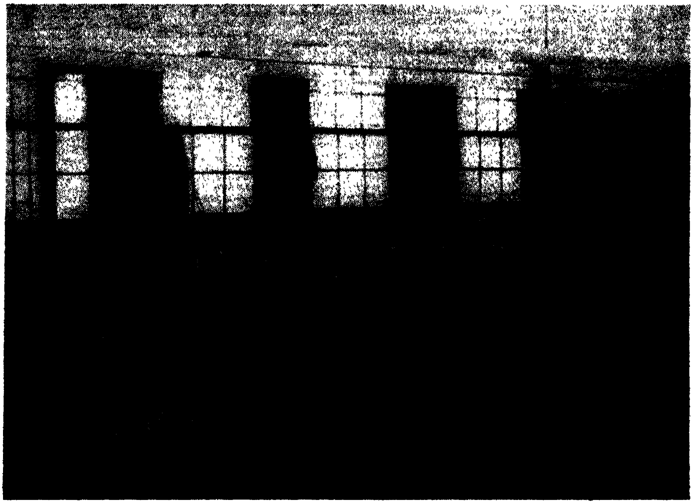
SKIN GREASES

Certain types of stock which are purchased from the glue manufacturer contain a high percentage of animal fat and it is, therefore, necessary to remove and purify this first as it constitutes the most valuable by-product.

Frizzings, or the fatty layers removed from sheepskin splits prior to dressing for chamois, contain a very high percentage of natural fat, and so do some of the waste materials from slaughter houses and butchers' shops. Extraction of fat from these materials is relatively simple. They should first of all be thoroughly washed, then preferably sliced or minced so as to facilitate extraction. Next the stock should be soaked in very hot water and then the fat extracted by pressure. To achieve this it is necessary to pack the material in canvas bags and to load up the press so that pressure is evenly distributed over the mass. The exuded fat is separated from the water and boiled up with open steam with 1½% concentrated sulphuric acid to break down the calcium soaps, the next operation is washing with several changes of warm water of 65° C. to remove all traces of acid, screening and filtration. If desired, physical bleaching may be resorted to but usually this is not necessary.

TANKAGE GREASES

From the evil smelling residue remaining in the glue pans after extraction of the grease, it is possible to recover some useful fat. The tankage may contain as much as 10–15% fat. One quite simple method which gives good results consists of boiling the mass with 2% concentrated vitriol for 3 hours in a lead lined tank, pressing the mass in a hydraulic press, and boiling up the fat with 5% sulphuric acid. After several boilings the grease is washed repeatedly with a succession of warm and cold waters, boiled up to remove excess of moisture, screened, filtered and finally barrelled.



Kettles, steam heated, 80 U. S. gallons used for recovering and refining glue greases.

CHAPTER X

PROPERTIES AND QUALITIES OF GLUE AND GELATINE

GLUE

A GOOD deal of useful information as to the quality, purity or source may be obtained by visual examination of representative samples. A high grade glue possessing good adhesive properties will be of a firm, solid nature, free from cracks and air bubbles and of a clear translucent appearance, unless, of course, it has been rendered opaque by some added coloring matter. Furthermore a good glue when fractured should not appear splintery but break off clear and clean. The appearance of splinters can usually be taken as a reliable indication that the glue has not been well boiled and possesses inferior adhesive properties. The color of glue varies from light amber to dark brown but it should never be black. Glue of a good quality will not possess a disagreeable odor when dry and should not develop such an odor after being 48 hrs. in solution. Light amber colored glue is usually of bone origin while the light and dark brown glues are the so-called hide glues derived from both hide and skin stock. Bone glues when examined by transmitted light frequently present a milky appearance due to the presence of suspended inorganic matter, particularly calcium phosphate.

The smell of a hot glue will often indicate the nature of the protein matter; hide pieces, pig's foot, bone and fish all possess definite and clearly distinguishable odors to the expert. There are several simple methods of differentiating between hide and bone glues.

E. Saver (Farben—Ztg., *31*, 721–2, 773–4, 1925) describes a simple distinguishing method. The ash of bone glue consists chiefly of phosphates, and the bulk is much greater than that obtained from incinerating hide glue. The ash from the latter is composed chiefly of calcium oxide and chloride. Hide glues are mostly neutral in reaction, whereas bone glues are more or less acid. Tannin solutions, such as sumac or gall nuts, may be used as a precipitating agent instead of sulphite waste liquors as prescribed by Stein (C.A. *17*, 2521) to distinguish between the two types of glue. A concentrated solution of tannin, and a small quantity of MgCl and AcOH are added to 1 per cent of glue at 50° C. Hide glue produces only a slight turbidity; bone glue, a brown, sticky precipitate. The action of alum on glue solution serves as a useful test. When 10 cc. of a glue solution of 30° C. are thoroughly shaken with 2 cc. of 5 per cent potash alum solution, gelatinization occurs in 1 to 2 minutes for hide glue, and there is no change if bone glue is present. With glue mixtures the time required for complete gelatinization is an indication of the relative amount of hide glue present. Iron alum has a stronger gelatinizing action than ordinary alum, and the yellow gel produced with hide glue is streaked with red and white, which serves as a further indication.

GELATINE

The purest gelatine is available in three different forms: flake, granulated and sheet. In the United States gelatine is usually ground to about 30 mesh, whereas in the United Kingdom the sheet form is common. It is colorless, tasteless and odorless and the sheet is of horny toughness. The specific gravity is 1.3. Gelatine possesses no definite melting point but begins to soften with decomposition at about 140° C.

The finest gelatine for eating purposes is made from calfskin as it retains its jelly strength longer than most other kinds. According to Dr. Werner Duecker of the Mellon Institute of Industrial Research, calfskin and bone gelatine set very rapidly, impart peculiar resilience to confectionery such as marshmallows and give appreciable strength. Pigskin gelatine does not retain its full strength on dilution and marshmallows are apt to become soft and have a slightly shorter life than have marshmallows made from other gelatines. In the case of photographic gelatines the nature of the original protein is of the utmost importance. Gelatine prepared from bones and from other sources is not so generally suitable for photographic work.

Rideal gives the following analytical results of four high grade British gelatines:

	Nelson		*Coignet*	*Swiss Gold*
	A	*B*	*Extra*	*Label*
Water	18.96	17.10	19.4	17.84
Ash	4.19	3.80	1.50	1.47
Gelatine (total N × 5.56)	76.73	78.26	78.34	79.67
Non-nitrogenous organic matter	0.12	0.84	0.75	1.02

The standards of the U. S. Joint Committee of 1907 give 2% as the maximum limit of ash and 15% as the minimum limit for nitrogen. These limits of 15% nitrogen and 2% ash correspond to a water content of 12% to 14%.

Winton, "Structure and Composition of Foods," gives the ultimate composition of two types of gelatine:

	Tendon Gelatine	*Ligament Gelatine*
Carbon	50.11	50.49
Hydrogen	6.56	6.71
Nitrogen	17.86	17.90
Sulphur	0.26	0.57
Oxygen	25.26	24.23
	100.00	100.00

The average moisture content varies between 10 to 17%. When placed in cold water, gelatine (flake, granulated or sheet form) swells by absorbing water from 5 to 10 times its original volume, depending on the temperature of the water and quality of the gelatine. When the swollen gelatine is warmed to about 40° C. it passes quickly into solution. An aqueous gelatine solution of 2 or more per cent will, when cooled to about 10° C., set to a firm jelly. This property of "gelling" is a valuable characteristic and several important commercial applications depend on the ability of 2–3 per cent solutions of gelatine to form firm jellies. According to H. R. Procter, "The Structure of Organic Jellies," Proc. Seventh International Congress of Applied Chemistry, London, 1909, a hot solution of gelatine may be looked upon as a true solution consisting of individual gelatine molecules, but the molecules orientate themselves, as the solution cools, so as to leave a minimum of free energy, the most active acid groups tending to unite with the most active basic groups until a continuous network is formed throughout the system. A block of jelly can, therefore, be considered as an enormous single molecule which in the presence of water is swollen as the solution fills up the interstices.

Gelatine is insoluble in alcohol and other well-known solvents but swells to a transparent jelly in the first-named solvent. According to Winton, "Structure and Composition of Foods," the specific rotatory power varies from 130 to

136°. C. R. Smith, "Jour. Amer. Chem. Soc.," *41* (1919), 135, suggests that gelatine exists in two forms: a sol form, having a specific rotation of $[\alpha]_D$ —141° and being stable at temperatures above 35° C., and a gel form, with a specific rotation of $[\alpha]_D$ —313° and stable under 15° C.; a condition of equilibrium existing between the two forms at temperatures between these extremes.

Of the common reactions for proteins, the xanthoproteic, Millon, sulphur and Adamkiewiez's reactions are faint and only decisive under certain conditions. Like the proteins, however, gelatine is precipitated by mercuric chloride, phosphotungstic and phosphomolybdic acids and gives the biuret reaction. Gelatine is not precipitated by lead acetate and copper sulphate, but with saturated picric acid it forms a precipitate. It may also be precipitated by saturation with zinc sulphate or ammonium sulphate. An acid solution of chromic acid precipitates gelatine, but not peptones. Platinic chloride will throw down gelatine. Potassium dichromate and formaldehyde react chemically, forming well defined compounds. Tannic acid precipitates gelatine from solution.

EVALUATION OF GLUE AND GELATINE

The most important tests are jelly strength, viscosity, moisture and ash. It is not proposed to describe the methods of testing as these are now standard for glue and gelatine as laid down by the National Association of Glue Manufacturers in the U. S. A. and by British Standard Specification Numbers 647 of 1938 for glue and 757 of 1937 for gelatine. For an excellent summary of the many mechanical devices for testing gelatine the reader is referred to Bogue's book which describes in some detail the work of Peter Cooper, Lipowitz, Valenta, Scott, Alexander, E. S. Smith, Forest

Products Laboratory, Hulbert, C. R. Smith, Shepperd and Schweitzer. References to jelly strength in this book are generally given as determined by the Bloom Gelometer.

It is customary for the glue manufacturer to control his production by the two main physical tests; jelly strength and viscosity and lots are not dispatched unless they conform to the minimum standards. Blending is carried out with flaked and granulated glues to ensure standardization of properties. In the case of edible or photographic gelatines evaluation is based on a number of factors:

1. Physical properties; jelly strength; viscosity; melting point; setting point.
2. (a) Ash content; constitution of ash, that is, whether metallic impurities are within the prescribed limits. (b) Sulphur dioxide.
3. Nitrogen content.
4. Gold number.
5. Bacterial count.
6. Acidity.
7. Mucin.
8. Grease.

For edible gelatine the last two tests are unnecessary as the presence of small quantities of grease or mucins, although undesirable, does not greatly interfere with its useful properties. Edible gelatine should contain only the merest traces of metallic impurities and sulphites. R. M. Mehurn (Ind. & Eng. Chem., 1923, *15*, 942, 3) found that the purest commercial gelatine containing only 10 per cent water; yielded on the average approximately 1.5 per cent ash. Of the heavy metals, iron occurs in the ash to the extent of 1.25 per cent; copper varies up to a maximum of 0.17 per cent. An average ash may be said to contain CaO, 53.46%; MgO, trace; FeO_3, 1.22%; P_2O_5, 5.4%; SO_3, 36.36% and SiO_2, 3.36%. Lange

(Ibid. 1909, *23,* 114) has reported up to 30 parts of AsO per million in edible gelatine and 0.02 to 0.467% sulphur dioxide.

The proportions of the "dangerous" metals should not exceed the following:

30	parts per million (copper)
100	parts per million (zinc)
1.4	parts per million (arsenic)

United States food laws lay down a maximum of 1.4 arsenic; 350 sulphur dioxide; lead nil; zinc 100; copper 30 parts per million.

E. Gudeman (Ind. & Eng. Chem., *1* (1909), 81) found that French gelatine (edible) contained 0.0260 per cent sulphur dioxide and American gelatine 0.0120 per cent SO_2.

From the food manufacturer's point of view the protective ability of gelatine in the production of oil in water emulsions is important and this can to a certain extent be gauged by its gold number. According to Zsigmondy the following gold numbers are attributed to the proteins; the smaller the number the greater the protective properties of the protein:

Gelatine	0.005– 0.1
Isinglass	0.01 – 0.02
Fresh egg white	0.08 – 0.15
Dextrin	10.00 –20.00
Potato starch	25.00

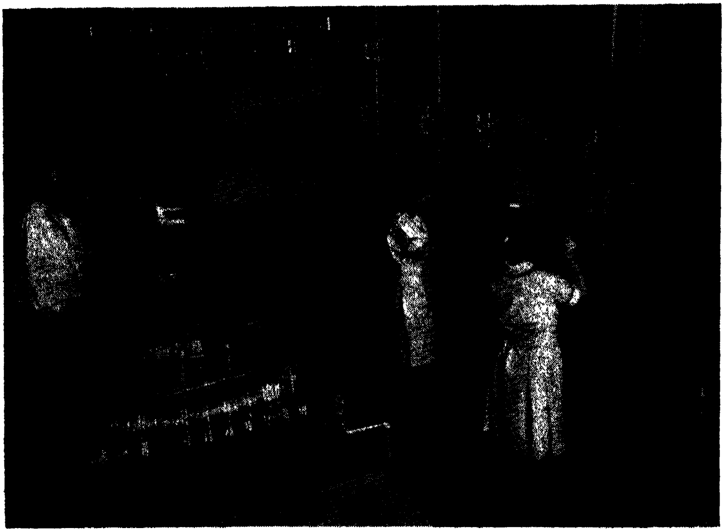
In consideration of the protective properties of gelatine as revealed by the gold number, it is important to remember that the efficiency of gelatine as a stabilizer depends to a large extent on its method of preparation. Gelatine prepared by acid treatment, i.e., possessing an isoelectric point at pH 8 requires pH 3 for the most efficient stabilization. Corresponding figures for the alkali-treated product are 4.7 and 1.0.

As regards acidity of the gelatine, Cattelain (J. Pharm. Chim., 1924, *49,* 444) states that the acidity calculated as HCl should not exceed 1.5%. The pH of the gelatine has a marked effect on its physical properties, for instance the melting point, which is constant at pH 5 and above, decreases between pH 5 and 2.5 and is again constant between pH 2.5 and 1.4. The swelling property and the viscosity are also affected. The normal pH of a good gelatine is 5 or 6. This is the usually accepted standard by British and American photographic equipment manufacturers.

The bacterial count for an edible gelatine must necessarily be very low and most manufacturers insist on a count below 30 per gm. Bogue gives the following amounts of bacteria in five representative samples:

1. 113,000,000 bacteria per gm. (inferior quality)
2. 14,000,000 bacteria per gm. (inferior quality)
3. 85,000 bacteria per gm. (fair quality)
4. 4,200 bacteria per gm. (fair quality)
5. 35 bacteria per gm. (good quality)

Referring briefly to the last two tests, namely grease and mucins, gelatine intended for photographic emulsions should contain no grease and a 2–5% solution of gelatine should give no precipitate when acidified with a 3% solution of acetic acid, thus showing that mucin is not present.



Gelatine Testing Laboratory.

CHAPTER XI

PLASTICS FOR GELATINE PLANT CONSTRUCTION

OF CONSIDERABLE interest to the gelatine industry are the many new developments which have taken place in the plactics industry during the last ten years. With the aid of plastics used either as plant components or as coatings for metal or brick pieces of equipment the manufacturer can prevent contamination of his product with injurious impurities and also effect worthwhile economies in his plant.

One of the most interesting plastic materials for the gelatine manufacturer is "Haveg" which is an asbestos filled phenol resin developed in Germany about 1923 by the Saureschutz Gesellschaft M.B.H. and since manufactured in one form or another throughout the world. This resin is unique insofar that it can be cold molded, use being made of cheap and easily accessible materials for building the molds such as wood, metal and even cloth. It is possible to mold a single piece tank 9 ft. in diameter and 9 ft. high with the aid of wood entirely. These large vessels do, however, require some kind of exterior mechanical reinforcement, such as wooden staves and steel bands. The physical properties of "Haveg" are sufficient for most purposes. Tensile strength 2,500 lbs. per sq. in.; transverse 5,500 lb. per sq. in. and compressive 10,500 lb. per sq. in. The resin has certain physical limitations, that is, it cannot normally be held to close dimensional tolerances and its low coefficient of heat transfer precludes its use in heat coils or steam jackets. Maximum temperature resistance is in the neighborhood of 135° C. Chemical resistance of "Haveg" is excellent and it will stand up to boiling hydrochloric acid without deterioration. The only chemicals it is not resistant to are: acetone; chromic acid in high concentrations; nitric acid; organic bases such as pyridine; caustic soda and potash, sodium hypochlorite and hot, concentrated sulphuric acid. Hydrofluoric acid attacks the asbestos filling.

There are available a number of cold setting cements of the type of "Haveg" which are suitable for lining tile or brick pits, etc., and when used in conjunction with a suitable hardener give a vitreous coating possessing high resistance to chemical attack.

It is suggested that "Haveg" tanks would be of great value for liming, washing, acid deliming and swelling gelatine stock, also for cooling pans where these are used.

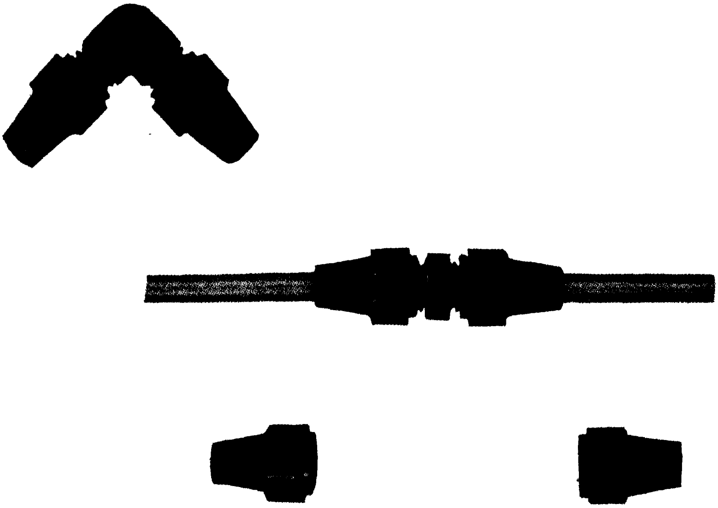
For the protection of steel or iron plant, particularly metal corroded and worn by long exposure to corrosive conditions, such as evaporating or extraction pans, etc., the use of a phenol formaldehyde varnish, "Lithcote," or similar preparations, is recommended. The film is 3/1000 in. thick and adds only 1/20th of an ounce per sq. ft. of treated metal. It stands up well to abrasion and the metal may be drilled and worked without breaking the film.

Method of coating the metal vessel is as follows: The surface is first cleaned and thoroughly dried, then a suitable phenolic varnish in alcoholic solution is sprayed onto the steel and the film polymerized by hot air. The vessel is well lagged during this polymerization and the temperature is very carefully controlled. When properly cured, the protective coating is exceedingly tough and able to stand up to very hard usage without cracking, crazing or chipping. It is particularly resistant to all weak acids as well as alkalies and is not affected by temperatures exceeding 100° C.

As a means of increasing the life of metal plant and also preventing contamination of the gelatine by metallic impurities there is no doubt that this type of plastic coating has very important advantages, particularly in wartime.

For protecting metal plants used in cold processing, polyvinyl resin may be employed. It can be sprayed on in the form of a solvent solution and applied by means of the Schori dry powder gun. This type of thermo-plastic is exceedingly tough and retains its useful properties even at low temperatures. Vinyl extruded tubing is recommended for consideration in place of copper or special alloy tubing and, provided it is not used for high temperature liquids, is eminently suitable. Vinylidene chloride polymer is a good example of the new plastics. This material in extruded form when used for conveying aqueous solutions, oils, etc., offers the highest resistance to moisture, 0.00% gain in 24 hrs., great toughness and abrasion resistance and ability to stand up to a great number of corrosive chemicals and solvents; also complete non-inflammability, high dielectric strength and ease of manipulation. The tubing retains its mechanical properties for long periods of time. For example Saran ¼" O.D. tubing with a 0.035" wall showed no tendency to collapse within 3 hours at 300° F. and 1 m.m. absolute pressure. This tubing did not bulge or rupture when heated to 212° F. and subjected to 200 lbs. per sq. in. air pressure for 13 hours. The resin is completely resistant to weak and strong acids and weak acids and strong alkalies. Available in transparent or opaque forms.

Pieces of plant may be machined of laminated phenolic plastics which possess exceptionally good mechanical and chemical properties and components may also be molded of standard or special molding powders.



New plastic corrosion-resisting fittings made of Saran.

CHAPTER XII

GLUE AS AN ADHESIVE AND MISCELLANEOUS APPLICATIONS

THE mechanism of glueing is difficult to explain and although several ingenious and comprehensive theories have been evolved there is, as yet, no really adequate explanation able to cover all phases of adhesion. The most acceptable theory of adhesion shares the view that two definite forces are brought into being, namely specific adhesion, involving a force of attraction between adhesive and surface, and mechanical adhesion, involving the embedding of solidified adhesive in the cavities of a porous material. Bancroft, Applied Chemistry, *1*, 74, 1924, is of the opinion that adhesion, in general, depends largely upon the degree of absorption of glue by the surfaces to be joined. McBain and Hopkins, Second Report of the British Adhesives Research Committee, favor the view that in the case of wood joints adhesion is mechanical. On the other hand, F. L. Browne and T. R. Truax, U. S. Forest Products Laboratory, Colloid Symposium Monograph, Vol. *Ix*, 1926, have produced evidence to show that mechanical adhesion and specific adhesion are operative in the glueing of wood commonly used by wood workers. They state, however, that specific adhesion between glue and wood does not presuppose absorption of the glue from the sol by wood. Browne and Truax are of the opinion that the properties required of a material to be useful as a glue for joining woods are such as are peculiarly characteristic of the emulsoid colloids which give elastic jellies and their definition of a glue is as follows:

> Any material which can be obtained as an emulsoid sol of suitable consistency, which wets a particular surface, and which subsequently forms a strong jelly by cooling, heating, evaporation and chemical reaction must be regarded as a glue for that surface.

There is, unfortunately, no single property of the glue which will give a reliable index of its adhesive properties. A true indication of adhesive or glueing ability can, however, be obtained by carrying out simple tests such as the "lap" or "shear block" but it is necessary that the conditions of the test are most carefully controlled. Some idea of the variable factors which influence adhesion, i.e., strength of joints effected, is given by the following:

GLUE

Concentration
Temperature and time of heating

TIMBER

Density and porosity
Presence of natural oils and gums
Moisture content
Surface finish
Grain direction and inclination
Temperature at time of glueing

GLUEING CONDITIONS AND PROCEDURE

Temperature and movement of air in the assembly room
Humidity of air
Time of assembly
Intensity of pressure applied to joint
Method and uniformity of glue application

Elimination of air bubbles
Duration of conditioning
Temperature and humidity of conditioning chamber
Dimensions of test piece

TESTING

Types of grips
Distance between jaws and pivots of grips
Rate of loading during test
Eccentricity of loading
Temperature and humidity at time of test

In connection with tests carried out to determine the strength of joints W. D. Douglas and C. B. Pettifor, Testing of Adhesives for Timber, Royal Aeronautical Society, Feb., 1929, point out that the complete elimination of timber failure is regarded by some authorities as impossible since the strength of high grade adhesives, such as hide glue, may be considerably greater than that of timber. The tensile strength of hide glue is 12 to 13,000 lbs. per sq. in.; the tensile strength of walnut parallel to the grain is about 24,000 lbs. per sq. in., but in the radial and tangential directions of the grain it is only 1,600 and 1,080 lbs. per sq. in. It is only to be expected that the nature of the glue influences the strength of joints. There is, for instance, a considerable difference between hide and bone glues as revealed by the following figures:

TENSILE STRENGTH

(1 pt. glue and 2 pts. water)

	Lbs. per sq. in.
Hide glues I	1,390
Hide glues II	1,390
Hide glues III	1,355
Bone glues I	851
Bone glues II	829
Bone glues III	439

Glues of one type from different sources also differ, but on the whole it can be taken that if the physical constants of the sample are high, i.e., if the jelly strength and viscosity are above the average, then it may be reasonably assumed that the adhesive properties will be good. It is, however, pointed out that special glues are developed for special purposes; whilst a high viscosity glue may be necessary for certain kinds of woodwork, for others a low viscosity adhesive might be required.

In practice the wood worker takes certain clear-cut precautions to ensure good adhesion. These may be summarized as follows:

1. Choice of good quality glue.
2. Use of a water or steam jacketed bath for melting.
3. Temperature control of melting, taking care not to exceed 65° C.
4. Evaporation of water from open glue pots made good by additions.
5. Use of clean utensils and prevention of hydrolysis due to putrefaction by addition of preservatives.
6. Moisture content of wood 13–17%.
7. Control of thickness of glue film to ensure that there is sufficient for the purpose.
8. Control of shop temperature and humidity.
9. Interval between application of glue and application of pressure.

For certain woodworking jobs additional safeguards are needed, thus in the case of glues for plywood manufacture it is essential that the glue should be of such a consistency that maximum spreadability is obtained.

Animal glues are used as adhesives for wood, paper and textiles. Veneering requires the highest grade of glue with a rising tensile strength and high viscosity. The glue must be free from color and grease and contain no hardening materials liable to interfere with the prompt adhesion of the glue to the base wood. It is important that the glue should not form a foam as this lowers its setting property and may even injure the delicate light wood veneers.

Although animal glues are seldom used for aeronautical purposes, preference being given to casein, urea formaldehyde, and phenolic glues owing to their resistance to moisture and dimensional changes due to moisture absorption, the old standards for animal glues adopted by the British Engineering Standards Association are of interest.

Class	*Breaking Stress*	*Use*
Propeller glues	1,100 lbs. per sq. in.	Airscrew manufacture
Class 1	1,000 lbs. per sq. in.	Important stress bearing work
Class 2	900 lbs. per sq. in.	Non-stress bearing work

Very considerable quantities of low grade glue are used in the manufacture of cardboard containers and cold fish glues are preferred by many concerns as they do not require preparing for use and this enables worthwhile economies to be effected in the assembly room.

Most of the trouble in the factory is caused by two factors:

1. Neglect to see that the glue boxes are regularly cleaned out.

2. Neglect to ensure uniformity of glueing conditions.

It is customary to add small quantities of antiseptics to the glue when it is used for bookbinding purposes so as to prevent insect damage. Numerous chemicals have been recommended, such as a mixture of mercuric chloride and iodide; 3 per cent of the chloride and 1 per cent of the iodide on the weight of the glue used. Other suitable antiseptic bodies are thymol; sodium benzoate; sodium salicylate; β-naphthol; phenol, parachlorometacresol; ethyl hydroxybenzoate, etc.

Rideal (Glue and Glue Testing) gives the following recipes for bookbinder's size:

No. 1. Water 1 quart; powdered alum ½ oz.; Russian isinglass 1 oz.; curd soap 20 grains. Simmer for one hour, then strain through linen or a fine sieve and use whilst still warm.

No. 2. Water 1 gallon; best glue ½ lb.; alum 2 oz. Prepare and use as above.

No. 3. Water 1 quart; isinglass 2½ ozs.; alum 120 grains.

MISCELLANEOUS APPLICATIONS OF GLUE

It is surprising to note the number of uses now being found for glue in modern industry. These include manufacture of matches, printers' rollers, electrolytic refining of metals, electro-plating, for insecticides, and for stabilizing foam in foam fire extinguishers, etc.

Large quantities of high grade glue are used in the production of printing rollers and hectograph plates.

Rideal gives the following recipes for printing rollers:

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Glue	8	10	4	2	32	2	1	3
Treacle (Molasses)	12	..	8	1	12	6	2	8
Paris white	1	..	..	..	..	..	..	1
Sugar	..	10	..	..	..	..	..	..
Glycerine	..	12	..	..	56	..	..	..
Isinglass (Oz.)	..	1½	..	..	..	..	..	..
India-rubber in Naphtha	..	..	..	..	10	..	..	..

Formaldehyde is frequently added to prolong the life of the roller, as it renders the gelatine insoluble in water.

F. Steinitzer (Kunstoffe, *4* (1914), 161) gives the following details concerning the composition of hectograph plates:

Glue or gelatine	15	10.0	25	10
Glycerine, 30° Bé.	60	50.0	90	50
Kaolin, Kieselguhr, etc.	..	2.5	10	10
Sugar	..	...	10	..

Bogue mentions that a small amount of some hardening agent, such as bichromate, alum, or formaldehyde is usually added.

Other uses for glue are in the manufacture of wallpaper, the sizing of textiles, and in the preparation of various artificial products, such as imitation leather, ivory and mother-of-pearl.

In the first instance the glue is used as a binder for the clay and other materials with which the papers are grounded. Glues to be incorporated with paper should be free from grease, of a good clear color, and form no foam. Viscosity is very important, as it determines the covering property of the glue.

Bogue writes:

> In the selection of the glues that will be satisfactory for use upon wallpapers, the greatest diversity of possibilities which may make a given glue excellent or worthless for the purpose present themselves. In fact, for no other service for which glue is employed is the exact nature of the materials, both of the colour bases and the glue itself, so necessary to take into consideration.

The usual method of making sized paper entails a final coating of glue, instead of adding it to the beater, together with the pulp and pigments, etc.

Good quality hide glues are used in the finishing of certain textiles. Thus, cotton goods are generally treated with a dilute solution of glue or gelatine in order to stiffen them, while carpets, curtains, etc., are heavily loaded with glue. In all these cases the glue used is derived from hide offal, and of a lower grade than that employed in sizing paper. The glue must be neutral, as the presence of acids and alkalies will affect the colors, and the inorganic ash should be low, as large amounts of neutral salts will affect the dyes.

Glue is also used for the quick precipitation of materials which settle very slowly from suspension. British Patent No. 500,453, taken out by English Clays Iovering Pochin and Co., Ltd., 1939, describes one such application. The example given states that 20 lbs. glue powder are allowed to swell in 20 gallons of cold water for 4 hours, the mixture is then heated to 60–70° C., diluted with 80 gallons of cold water and kept for 16 to 24 hours. One-half gallon of the solution is used to one ton of clay dispersed in water and assists materially in increasing the rate of precipitation.

An interesting example of the use now being made of glue for coating purposes is afforded by British Patent 501,558 taken out by Atlas Powder Co. in 1939. Fibrous material is rendered impervious to oil, grease and hydrocarbons by two superimposed coatings, whereof the first is highly resistant to moisture and consists essentially of plasticized cellulose derivatives and the second coating is highly resistant to oils, greases and hydrocarbons and consists essentially of a water soluble organic binder, e.g. glues and gelatine, which has been improved in flexibility by the addition of at least 60% sorbitol. The use of the prepared material is suggested for oil containers.

The use of gelatine in conjunction with plastics is of interest. The British Adhesives Committee mention special adhesives useful for joining incompatible solids which can be prepared by dissolving cellulose acetate in pyridine and adding this to an acetic acid solution of a high grade hide glue. The writer has seen a number of examples of molded glue and phenolic resin mixtures. The great disadvantage of such mixtures is that they are very prone to undergo considerable dimensional changes due to absorption of moisture.

CHAPTER XIII

GELATINE FOR THE PHOTOGRAPHIC INDUSTRY

THE chief requirements of a photographic gelatine are purity (that is freedom from suspended matter, from dirt in the nature of grease); freedom from a serious proportion of degradation products which may be formed in the actual manufacture of the gelatine; freedom from color; freedom from excessive acidity or alkalinity; freedom from insoluble particles (gelatine itself may easily be rendered insoluble by overheating in the drying process); and freedom from adulterants such as antiseptic agents, or hardening agents, such as chrome alum. According to the Report of the British Research Committee on Adhesives the gelatine for photographic emulsions should possess a high jelly strength (130–160) equal to or greater than the highest Cooper grades. The moisture limit is given as 8–15% and it is stated that more than 15% indicates a bad keeping quality whilst below 8% indicates an overdried gelatine possessing poor swelling properties. The limit for ash is 2%; iron and copper not exceeding 50 to 60 parts per million; lead not over 50; sulphur dioxide not exceeding 0.1% and ammonia not more than a trace. The Reports state that the gelatine should not reduce ammoniacal silver nitrate in the dark in 12 hours. Grease and mucin must be nil. There is only one reliable test for gelatine and that is to make a batch of emulsion with a sample of it under normal factory conditions. Such a test reveals at once the suitability of the particular sample for the regular emulsion. The fact cannot be too greatly stressed that the nature, as distinct from the purity of the gelatine, plays a vital part in influencing its suitability for sensitive emulsions. In a communication to the author when the first edition of this book was published, Messrs. Ilford, Ltd., the well-known British manufacturers of sensitized materials, stated that there appear to be several different gelatines, varying appreciably in chemical constitution, and the various sources of gelatine do not produce the same modifications, or produce them in different proportions. The question of purity is, therefore, somewhat misleading as it is not so much a question of actual purity, although this is important, as of the chemical and physical nature of the gelatine. Gelatines required for different processes do vary, but the precise nature of the variation is not yet known. A gelatine suitable for one emulsion is not necessarily suitable for another emulsion, and the differences lie between the emulsions rather than between the purposes for which the emulsions are required, that is to say, whether for plates, films or papers.

It well repays the gelatine manufacturer specializing in the production of photographic gelatines to utilize one proved type of stock and secure it from one or two known reliable sources. European manufacturers are of the opinion that hide bellies and shoulders from the sole leather manufacturer give the best results and, as mentioned at the commencement of this book, a general practice is to dry the stock and ship it to the plant in barrels. Strictly speaking it would be preferable for the manufacturer to purchase his stock in the raw, that is, unlimed condition and to carry out for himself the necessary processes of unhairing, liming, etc.

A recent U. S. patent, 2,191,034, taken out by S. E.

Sheppard and J. H. Hudson, Eastman Kodak, covers the above suggestion. The method is devised so as to produce a gelatine having an isoelectric point in the region of pH 6 to 9. The hide is dehaired in a ¼% to 1% alkaline solution containing 1% to 10% of neutral salt to prevent swelling of the hide material, then removed, washed and plumped in an acid bath; the hide substance neutralized to a pH of about 5 to 7 and the gelatine extracted in the usual way. Only by such means as the above can the photographic manufacturer be assured of perfect standardization of properties. If the gelatine manufacturer purchases his stock willy-nilly he can never be certain that at least a portion will not contain dangerous impurities such as fluorides used now as preservatives in salting, or that arsenical cures and depilatories will not increase beyond the safe limit the proportion of As_2O_3 in the ash. More important than this is the difference in the physico-chemical properties of gelatines from hide, calf, pig, sheep, goat and rabbit skins. Only by complete standardization of stock can the gelatine manufacturer hope to produce the very high quality product necessary for the photographic industry. In Great Britain there has been for a number of years some confusion of thought regarding the type of gelatine best suited for emulsions. Manufacturers have been under the erroneous impression that a gelatine possessing a low mineral ash and the required physical properties must necessarily be entirely suitable for emulsion making. They have persistently ignored the importance of the nature of the protein and disregarded the fact brought out by the result of experience, that certain types of gelatine, no matter how pure or how closely they conform to physical standards, are not always capable of making first class emulsions. Blended gelatines are not recommended for the preparation of emulsions and the gelatine should come from one known source approved by the buyer as the most suitable.

Considering the formation of photographic emulsions, D. F. Bloch, in his Streatfeild Memorial Lecture, 1927, "The Chemist in the Photographic Industry," gives the following excellent description:

> Roughly speaking, the emulsion is prepared by adding silver nitrate to a warm solution of gelatine in water containing an excess of soluble bromide, a little iodide being usually present, and more or less ammonia. The silver halide, which is submicroscopic at the time of formation, grows during the digestion which is subsequently given, the operation being termed ripening. In the absence of a silver solvent the grains of halide do not grow. How do they grow? By aggregation crystallization, i.e. the adhesion of clumps to form a crystalline aggregate? by a process of solution of either the smaller or more soluble grains, or by the possible formation of colloidal silver in the grains, which might afford crystallization nuclei? Or, if the solution velocity of colloidal silver bromide is greater than that of crystalline silver bromide, there would be a tendency to form the latter. Even at this early stage, we are in some doubt as to the rationale of the process. Ripening is carried on for some length of time necessary to endow the emulsion with such potentialities as may be desired within the limits of its capacity, and during this time the halide grains increase in size. The emulsion is set, shredded, and washed, and may subsequently be further digested, during which process its latent capacities can be exploited to a greater or less extent. If, at any stage, the processes are pushed too far, the emulsion tends to give fog upon development, i.e. the difference between the unexposed and light exposed halides grows less. Plain silver bromide precipitated in the dark is at once reduced by developers of normal strength, but it is possible to develop a latent image from it after exposure by the use of a very dilute or an acidified reducing agent. In the emulsion the colloid acts as the protecting medium, making it possible to develop the latent image, but if the emulsion be left in the developer for a considerable length of time reduction gradually takes place. Thus, in the case of fast emulsions, we are working upon the borderline of fog; and it is not a little remarkable that a product of such a character should retain its properties unimpaired over a long period of years. The emul-

sion, once made, is coated upon a suitable base, and the pretreatment of this base, the spreading and drying of the emulsion, often present difficult problems to the chemist and engineer.

The principal action of gelatine is protective; quite possibly it may act as an absorbent for the halogens, but this is by no means proven. Recent workers, notably Renwick, suggest that in the complex silver bromide grain, highly unstable silver occurs in solid solution. On exposure to light in the usual manner this changes into an "electrically neutral form of colloidal silver," which, owing to its fine dispersion, is capable of acting as a catalyst for development, accelerating the coagulation of the silver. The idea of "light sensitive silver nuclei" is a comparatively recent theory, and much work is now being done along these lines.

Sheppard and his co-workers have done much work upon the isolation of the actual "sensitizer" in the gelatine. They examined large quantities of deliming liquor from the gelatine factory, and found that there was present a small amount of a chemical which conferred high sensitivity to the emulsions made from purified gelatine. This chemical, allyl isothiocyanate ($C_3H_5N:C:S$), exists in normal gelatine at a concentration of from 1 : 300,000 to 1 : 1,000,000. Allyl isothiocyanate, commonly known as allyl mustard oil, is one of the best examples of the isothiocyanates. On hydrolysis they yield primary amines

$$S:C:NR + H_2O \rightarrow RNH_2 + COS$$

and also on reduction

$$S:C:NR + 4H = NH_2R + CH_2S$$

It should be remembered that the thiomethylene formed in the last reaction polymerizes to $(CH_2S)_3$ almost immediately.

In discussing the action of this agent, Bloch gives a brief summary of the supposed mechanism of its action as a sensitizer:

> It is believed that the isothiocyanate is converted into this—carbamide. This is known to combine with the silver halides to form complex compounds which, in alkaline medium, break down, yielding silver sulphide; these, it is suggested, form the sensitivity nuclei, and if they attain more than a certain dimension yield fog upon development. A soluble sulphide cannot form these nuclei, since it acts at once and directly upon the silver bromide grain, giving silver sulphide without nucleus formation by means of an intermediate complex.
>
> The sulphide is supposed to act as a nucleus in the reduction on development, and it is suggested that it deforms the lattice structure of the silver bromide—but this is speculation. The existence of definite nuclei at which development starts seems to be fairly well established, but the evidence for the existence of sensitivity nuclei is not convincing. It is not known, for instance, whether the silver sulphide specks themselves behave as light sensitive centres, or whether they act indirectly by promoting local instability, though the latter seems the more probable explanation.

Gelatine is useful for making light filters on account of the fact that colored glass is liable to refract the light that passes through it more or less unevenly. A variety of colors can be used when gelatine is employed, as this material dyes very readily, whereas glass is difficult to color the correct tint. Gelatine films are best mounted between optical flats.

PHOTO-LITHOGRAPHY

The process of photo-lithography depends upon the action of light on chromed gelatine. Thus gelatine is treated with a strong solution of potassium bichromate in the dark and exposed through a photographic negative to a strong light. Formerly, the jelly was formed on a glass plate, but at the present time, zinc is used for this purpose.

The action of light is in principle fairly simple. Where the negative is "thin" and the light can penetrate to the jelly, the gelatine will be rendered insoluble, whilst the dense parts of the negative protect the gelatine and light has little effect upon it. Gelatine affected by the light will not swell, and vice versa. A mirror copy of the negative is thus produced on the film of gelatine. The plate is usually covered with graphite and a plate of copper deposited upon it in an electrolytic solution.

The two- and three-color process involves complications into which the author cannot enter at this stage. The secret of photo-lithography lies in the formation of the photo-sensitive chromo-gelatine.

Bogue gives the following equation as typifying the reaction:

Bichromate, first reduced by the action of light on gelatine, forming the chromium sesquioxide.

$$K_2Cr_2O_4 \rightarrow Cr_2O_3 + K_2O + 3\,O.$$

Oxygen absorbed by gelatine participates in its insolubilization. The potassium oxide is, of course, changed to the hydroxide, and reacts with more of the bichromate with the formation of chromate,

$$K_2Cr_2O_4 + 2\,KOH \rightarrow 2\,K_2CrO_4 + H_2O.$$

The neutral chromate acts on the gelatine in the presence of light in a manner quite similar to that of the bichromate, but with extreme slowness,

$$2\,K_2CrO_4 \rightarrow Cr_2O_3 + 2\,K_2O + 3\,O.$$

Finally, the sesquioxide reacts with the excess of bichromate to form chromium chromate,

$$K_2Cr_2O_4 + Cr_2O_3 \rightarrow CrO_3 + Cr_2O_3 + K_2CrO_4.$$

In the opinion of Bogue, the above equations, due to

Lumière and Seyewetz, need some revision. Thus he suggests that the last equation might be better written:

$$
\begin{aligned}
&K_2Cr_2O_4 \rightarrow K_2CrO_4 + CrO_3.\\
&3\,CrO_3 + Cr_2O_3 \rightarrow Cr_2(CrO_4)_3.\\
&2\,Cr_2(CrO_4)_3 \rightarrow 5\,Cr_2O_3 + 9\,O.
\end{aligned}
$$

Gelatine is used in the modern collotype process to an appreciable degree. The faults ascribed to it, however, are irregularity and slowness of printing.

There is no doubt that the irregularity arises from a perfectly natural cause, namely, that an equilibrium of swelling has to be maintained in an unstable substance whose capacity for absorption is influenced, to an appreciable degree, by external factors.

Success depends upon the choice of the gelatine, the strength of the sodium or potassium bichromate, and the exposure. In collotype printing, it suffices for the moistening of the plate after each print to use an ordinary damping roller as in lithography.

CHAPTER XIV

GELATINE IN THE FOODSTUFF INDUSTRY

DR. T. B. DOWNEY of the Mellon Institute of Industrial Research states that gelatine is a very valuable addition to dietary for the following reasons: "easy digestion and ready absorption; protein saving ability, efficient aid in the digestion of other foods (with particular reference to milk and milk products), remarkable supplementary value when fed with many protein foods, useful physiological effects and unique property of forming the basis of many dishes, exceptionally attractive in appearance and appealing to the taste." Gelatine is one of the easiest proteins to digest and its cleavage products are very completely absorbed by the system. Dr. Downey points out that the enzyme pepsin of the gastric juice working in an acid medium converts gelatine into the corresponding proteoses and peptones; while trypsin in the pancreatic juice, breaks up the molecules into the corresponding amino-acids with great rapidity.

The term incomplete protein is usually given to gelatine because its cleavage or hydrolytic products do not contain all the amino acids necessary for a healthy protein diet. Those amino acids absent from gelatine are tryptophane and oxyglutamic acid and the amounts of cystine and tyrosine are small as compared with other complete proteins.

TABLE FROM SHERMAN'S "CHEMISTRY OF FOOD NUTRITION"

Amino Acid	*Gelatine*	*Casein (Milk)*	*Gliadin (Wheat)*	*Zein (Corn)*
Glycine	25.50	0.49	0.00	0.00
Alanine	8.70	1.85	2.00	13.89
Valine	1.00	7.93	3.34	1.88
Leucine	7.10	9.70	6.62	19.55
Proline	9.50	7.63	13.22	9.04
Oxyproline	14.10	0.23	?	?
Phenylalanine	1.40	3.88	2.35	6.55
Glutamic acid	5.80	21.77	43.66	26.17
Oxyglutamic acid	0.00	10.50	2.40	2.50
Aspartic acid	3.50	4.10	0.58	1.80
Serine	0.40	0.50	0.13	1.02
Tyrosine	0.01	6.50	3.50	3.55
Cystine	0.31	0.50	2.32	0.85
Histidine	0.91	2.84	3.35	0.82
Arginine	8.22	3.81	3.14	1.82
Lysine	5.92	7.62	0.92	0.00
Tryptophane	0.00	2.20	1.14	0.00
Ammonia	0.49	1.61	5.22	3.64

In spite, however, of the fact that gelatine is an incomplete protein it is a most valuable addition to the diet and Professor E. V. McCollum of Johns Hopkins University has stated that gelatine is more efficient in promoting growth and health than casein, which is a complete protein.

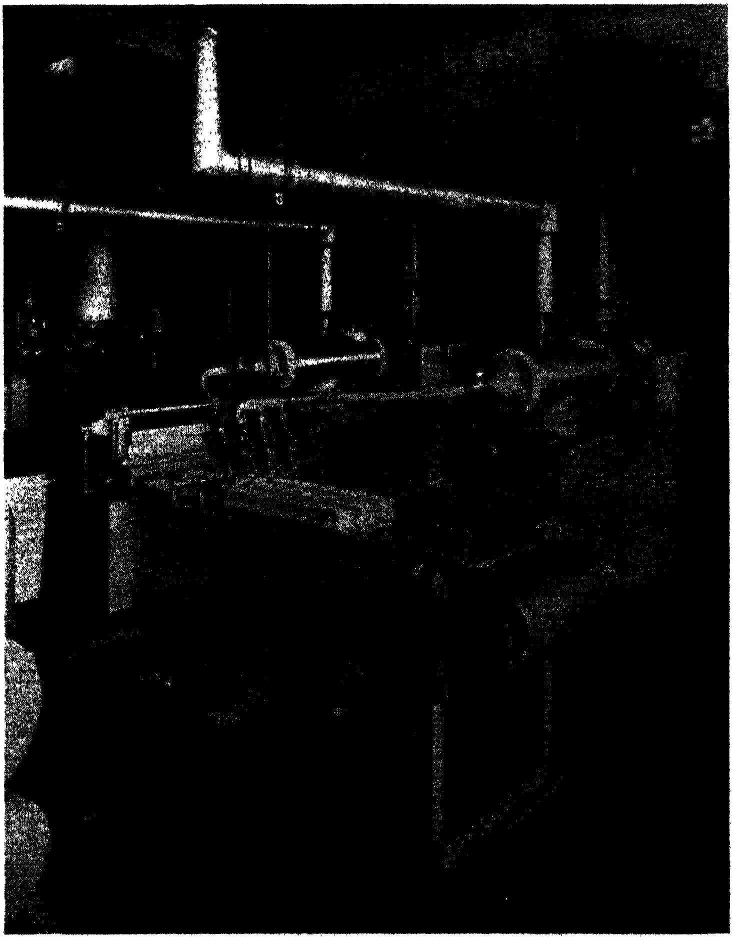
Gelatine finds the following applications in the food industry:

1. In ice cream manufacture as a stabilizer preventing the formation of large ice crystals and as a means of increasing viscosity of the mix, improving the body texture and appearance, particularly after holding for several days.

2. As a protective colloid in the production of infants' food.

3. In confectionery manufacture for giving permanence to candy and for the prevention of large sugar crystals.

4. As a "gelling" medium in table desserts, meat extracts and meat preparations.
5. As a thickener in jellies, jams, fruit preserves, etc.
6. Emulsion stabilizer for salad creams, etc.



Extruding ice cream.
Gelatin is now commonly used in ice cream manufacture.

1. Considerable research work carried out at the Mellon Institute of Industrial Research has shown that the optimum percentage of gelatine in the mix is close to 0.4% and the granulated gelatine is preferably stirred in the cold solution and dissolved by pasteurization at 145° F., and the mixture then viscolized.

The following table showing the physical properties of ice cream as influenced by a medium test gelatine gives the results of tests carried out by Dr. T. B. Downey of the Mellon Institute. The gelatine used gave a reading of 160 G on the Bloom gelometer at 10° C. in 14 to 1 concentration. The ice cream mix contained 36 to 40% total solids consisting of 12% butterfat, 10% of milk solids, no fat and 14% sugar. The mix was pasteurized for 30 minutes at 145° F.; viscolized at 2,000 lbs. pressure; aged for 48 hours at 40° F., and then frozen.

PHYSICAL PROPERTIES OF ICE CREAM AS INFLUENCED BY MED. TEST GELATINE

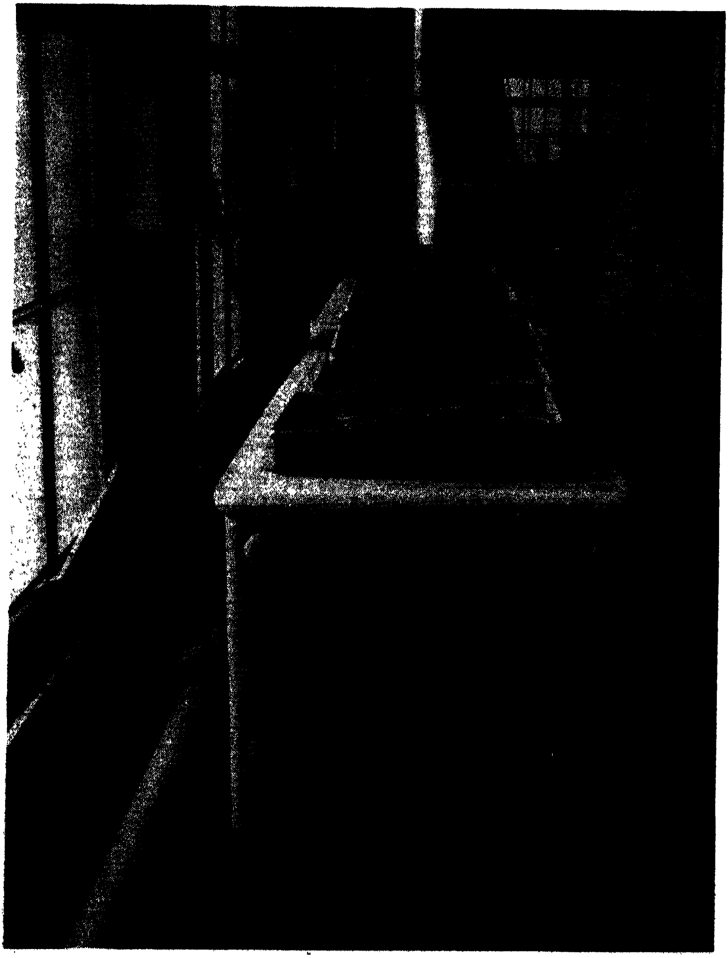
Percentage of Gelatine in Mix	*Viscosity of Mix with Stormer in Sec. at 10° C.*	*Degrees MacMichael at 9° C.*	REMARKS ON FREEZING	
			Attain Overrun	*% Overrun*
None	11	21	Very easy	90
0.3	14	33	Very easy	90
0.4	19	60	Very easy	90
0.5	30	130	Easy	90
0.6	48	220	Slow	80

Percentage of Gelatine in Mix	*Loss of Overrun During Hardening*	*On Dipping, % Loss, T. 10–12° F.*	*G. of Melt from 160 G. Ice Cream in 2 Hrs.*	*Appearance of Melting Cream*
None	Considerable	40	96	Very fast Thin
0.3	Considerable	38	91	Very fast Thin
0.4	Slight	30	83	Fast Fair
0.5	None	28	56	Good Smooth
0.6	Slight	26	42	Slow Lumpy

Percentage of Gelatine in Mix	*Quality of Product After 10 Days Holding, Body Texture*	*Texture After 30 Days Holding*	*Texture After 90 Days Holding*	*Choice of Product by Consumers in %*
None	Light	Very granular	.....	..
0.3	Light	Slight grain	Grain	..
0.4	Fair	Smooth	Slight grain	..
0.5	Good	Smooth	Very slight grain	75
0.6	Good Slightly gummy	Smooth	Very slight grain	25

2. The value of gelatine in the production of infants' foods is now well recognized by dieticians. J. Alexander (J. Amer. Chem. Soc., *32,* 1910, 680–87; P. B. Hawk, Proc. Soc. Exptl. Biol. Med., *20,* 1923, 269 and T. B. Downey, J.

Metabolic Research, S., 1924, 145) all believe that gelatine acts as a protective colloid in modifying the curd formation of the casein during digestion. This is by no means certain, but whatever is the action of this protein there is conclusive



Gelatine sheets ready for soaking in water preparatory to being used in the manufacture of marshmallows.

proof that it does achieve a most valuable purpose in easing the digestion of milk.

3. In the manufacture of candy, particularly marshmallows, gelatine gives permanence to the sweet and prevents the formation of large sugar crystals. According to Dr. Werner Duecker, Mellon Institute, see "The Manufacturing Confectioner," Nov. 1926, gelatine up to 0.9–1.0% increases crystallization but above this figure it decreases crystallization.

Scene in a large confectionery plant handling marshmallows and similar candies.

4. Meat extracts contain from 0.25 to 5.50 per cent gelatine. Rideal found in three well known "Invalid Jellies" the following amounts of gelatine: 5.15%; 5.48%; 4.11%. Table desserts contain 2.5 to 3.5% gelatine.

5. Gelatine finds a ready use as a thickener in jellies, jams, etc. Atwater and Bryant, Bulletin 28, U. S. Dept. of Agri-

culture, give the following analysis showing the amounts of gelatine shown as protein in two samples of cherry jelly:

	Total Solids	*Ash*	*Acids*	*Protein*	*Reducing Sugar*
Cherry jelly (a)	61.60	60.0	....	1.100	59.80
Cherry jelly (b)	79.00	70.0	....	1.200	77.20

6. Of growing interest is the use of gelatine in various emulsions where it helps by reason of its protective colloidal nature in preventing a premature breakdown of the emulsion. As mentioned previously, the efficiency of gelatine as a stabilizer depends on its method of preparation. Gelatine prepared by acid treatment, having an isoelectric point at pH 8 requires pH 3 for the most efficient stabilization; corresponding figures for the alkali treated product are 4.7 and 1. Exposure to ultra-violet rays causes increased viscosity but this is accompanied according to S. A. Reitlinger, Colloid Journal (Russia), *4*, 679 (1938), by diminution of the properties of swelling and solubility. U. S. Pat. 2,242,883 describes a method of improving the whipping qualities of gelatine by subjecting dried gelatine to the action of U.V. light.

Gelatine is used in the preparation of soups and meat teas, pork pies, brawn and similar meat foods. In household cookery gelatine is generally preferred as a "gelling" medium for a number of sweet and savoury dishes.

CHAPTER XV

MISCELLANEOUS APPLICATIONS OF GELATINE

PHARMACY; BREWING; BACTERIOLOGY; LEATHER FINISHING, ETC.

THE USES OF GELATINE IN PHARMACY

GENERALLY speaking, the ordinary commercial edible gelatine on the market is of no use for pharmaceutical purposes, a "super product" being essential for this work.

The large firms specializing in the manufacture of capsules, pastilles, suppositories, etc., generally buy gelatine on the results of detailed analysis as carried out by their chemists. First of all the buyers, sent out by the pharmaceutical manufacturers, examine the market for good stock, and then send samples of high-class gelatine to their employers for examination and approval.

Gelatine for suppositories must contain no string fibres. Where it is the practice to dry the gelatine on fibre netting instead of zinc, there is a great liability of stray wisps of string adhering to the surface of the gel.

A gelatine containing a trace of sulphites, but devoid of fibre, would perhaps be quite suitable for suppositories, whereas the presence of a little fibre would not matter, if the gelatine were to be used in the manufacture of pastilles; sulphites, however, would be distinctly objectionable. Air bubbles in gelatine are regarded with great disfavor. It is found that they affect the tensile strength to a considerable degree, and in the molding of capsules, etc., the gelatine, or rather glyco-gelatine, is apt to tear if air bubbles are present. Samples containing air bubbles are disregarded on inspection. For household use, leaf gelatine containing air bubbles would be quite suitable, provided, of course, that sulphites were absent and heavy metals below the approved standard.

As already indicated, tensile strength is always tested by the pharmacist. It is of vital importance that the glyco-gelatine should be able to withstand the tearing action of molding. Each manufacturer has his own particular tensile strength testing apparatus, and works according to the best conditions of his plant. Thus, after considerable experience, a workable figure is found, and this is rigidly adhered to; gelatine with a strength below this standard is rejected.

The mineral ash for gelatine used in pharmacy is 2 per cent maximum. Constituents of the ash which are particularly objectionable are the heavy metals, the most important being copper and arsenic. About two parts per million of these metals is the standard generally accepted. Sulphites are, of course, supposed to be absent from edible gelatine, according to recent Health Legislation, and although a trace is allowed in some cases, the presence of these chemicals denotes an inferior product.

The following tests are employed by the manufacturer before purchasing gelatine:

1. General inspection. Particular importance paid to color, air bubbles, cracks. Tensile strength.
2. Determination of mineral ash. (a) Estimation of copper and arsenic.
3. Sulphur dioxide estimation.
4. Acidity or alkalinity.

5. General qualitative tests sometimes applied first.

The following are stages in the manufacture of gelatine capsules:

1. The emulsion is prepared in tin-lined, copper, water-jacketed containers.

2. The properly prepared gelatine emulsion is run onto special stainless steel plates placed in position under the containers.

3. The coated plates are dried off in ovens.

4. Molds are in two parts. The film of clear gelatine is laid upon one half, the correct amount of medicament passed in and another gelatine film put on top. The other half of the mold is put in position and the whole compressed in the hydraulic press for a few seconds at 3,360 lbs. per sq. in.

Regarding acidity or alkalinity, the pH of the gelatine is usually determined. Acid gelatines are objectionable for lamellae, where small quantities of foreign impurities may pass into the medicament, which in the case of such substances as adrenalin and other alkaloids used for opthalmic preparations must be of unquestionable purity.

Dealing with the detailed application of gelatine in pharmacy, the first product containing quite appreciable quantities is the ordinary glycerine throat pastille.

The British Pharmaceutical Codex gives the following formula for Glycogelatinum:

GLYCOGELATINUM

Gelatine	12.00
Glycerine	40.00
Distilled water	20.00
Orange-flower water	20.00
Sugar	5.00
Citric acid	2.00
Oil of lemon	0.10
Solution of carmine	1.00

Soak the gelatine in the distilled water until quite soft, add the glycerine, heat gently on a water bath until the gelatine is dissolved, and add the orange-flower water, in which the sugar and citric acid have previously been dissolved; then add the oil of lemon and solution of carmine, mix thoroughly, strain through muslin, and allow to solidify.

Glycogelatinum is used as a basis for throat pastilles, the medicament being dissolved or suspended in the melted glycogelatine, the mixture poured into trays to solidify, and cut up into the required number of pastilles; or the melted mass may be poured into suitable pastille molds.

Pessaries and urethral bougies also contain proportions of gelatine.

GLYCERINE JELLY

I		*II*		*III*	
Gelatine	35 gm.	*Soft*		*Hard*	
Glycerine	450 gm.	Gelatine	15 gm.	Gelatine	25 gm.
Water	500 gm.	Water	30 gm.	Water	25 gm.
Salicylic acid	3 gm.	Glycerine	55 gm.	Glycerine	50 gm.

Soak the gelatine for half an hour in water, add glycerine, and heat until dissolved.

W. A. Poucher (Perfumes, Cosmetics, and Soaps, 1926, Vol. 2, page 350) suggests the following recipe for glycerine jelly.

Gelatine must be water-white and odorless. 2 per cent in warm water gives a jelly when cold, so that the consistency of any product can be based on the percentage used in comparison with this figure.

Gelatine	30 gm.
Glycerine	170 cc.
Orange-flower water—triple	800 cc.

Place the gelatine in 500 cc. water and let it stand overnight. Then warm till dissolved. Add glycerine and rest of water.

As gelatine, even the purest Gold Leaf, contains quantities of objectionable soluble salts, it is sometimes the practice to purify it if an extra pure product is desired, a water-white product being obtained. The best method is to soak the sheets in successive changes of distilled water for several days. The gelatine is disolved in hot water and filtered into absolute alcohol. The white mass is then re-dissolved in hot water, reprecipitated, and finally dried; the gelatine obtained in this way will contain as low as 0.4 per cent to 0.7 per cent ash.

F. Winter (Handbuch der gesamten Parfumerie und Kosmetik, 1927, page 326) gives the following recipe:

ZINC JELLY

Gelatine	15 gm.
Water	45 gm.
Glycerine	25 gm.

Add to this a mixture of

ZnO	10 gm.
Glycerine	15 gm.

and make up to 100 gm. with distilled water.

Pastes of gelatine with glycerine are made up containing zinc oxide, resorcin, and other medicaments for application to the skin in the case of skin diseases. A well-known paste of this kind is Ichthamol Paste.

ICHTHAMOL PASTE

Ammonium ichthosulphonate	10.00
Gelatine	10.00
Glycerine by weight	60.00
Distilled water	25.00

Gelatine dissolved in water, glycerine added, then the ammonium ichthosulphonate.

Other gelatine ointments are given by Winter, thus:

Zinc jelly	30 gm.
Rub in—	
Lanolin	48 gm.
Zinc oxide	20 gm.
Glycerine	20 gm.
Water	50 gm.

Incorporate medicaments by adding them first to the lanolin. Apply by melting and painting with a brush onto the skin, and then sprinkle lycopodium onto it. This gives a lasting, non-sticky film on the place of application.

Gelatine is used for pill coating, the following recipe being typical (Pharmaceutical Formulas, 1899, page 587):

Gelatine	2½ oz.
Gum acacia mucilage	1½ oz.
Boric acid	2 dr.
Water	7½ oz.

Other important applications of gelatine in pharmacy are in the preparation of formo-gelatine, an antiseptic product employed as a surgical dressing; also the manufacture of court plasters.

"Lamellae" are discs of gelatine with some glycerine, weighing from 1/50 to 1/30 gm., and containing a minute dose of some powerful alkaloid. They are dissolved in water for ophthalmic and hypodermic use; four kinds are specified in the British Pharmacopoeia.

The gelatine basis from which the pharmaceutical discs are made is prepared as follows:

Gelatine	10.50
Glycerine	1.25
Distilled water	82.25

The Pharmaceutical Codex gives the following formulae for important varieties of lamellae:

ATROPINE DISCS

Atropine sulphate, 13 mg.
Sufficient quantity of distilled water
Gelatine basis, 75 dg. (grains 115)

The above preparations are used in ophthalmia to dilate the pupil.

COCAINE DISCS

Cocaine hydrochloride, 13 dg. (20 grains)
Distilled water, a sufficient quantity
Gelatine basis, 5 gm. (77 grains)

Gelatine is sometimes used in cosmetic preparations. It forms a transparent, jelly-like mass which melts on the skin, and is used for chaps and sunburn. Glycerine, the principal constituent of these mixtures, is the healing agent. Manufacturers are finding that gum is more suitable than gelatine, as it tends to ooze moisture, i.e., in a collapsible tube, a drop of liquid often appears at the nozzle when the tube is squeezed. The following two recipes may be of general interest to pharmacists:

GELATINE CAPPING

Gelatine, 33 lb.
Soak for 1 hr. then dissolve by heat in 5 gal. of water
Add glycerine, 5 lb.

Stir in a sufficient quantity of coloring matter, such as burnt sienna or vegetable black, until the mass nearly sets. In use, warm till melted and dip bottle previously corked into the mixture.

WATERPROOF PAPER

Gelatine	10 gm.
Water	40 gm.
Glycerine	10 gm.

Paint both sides of paper (hot), cool and then cover with

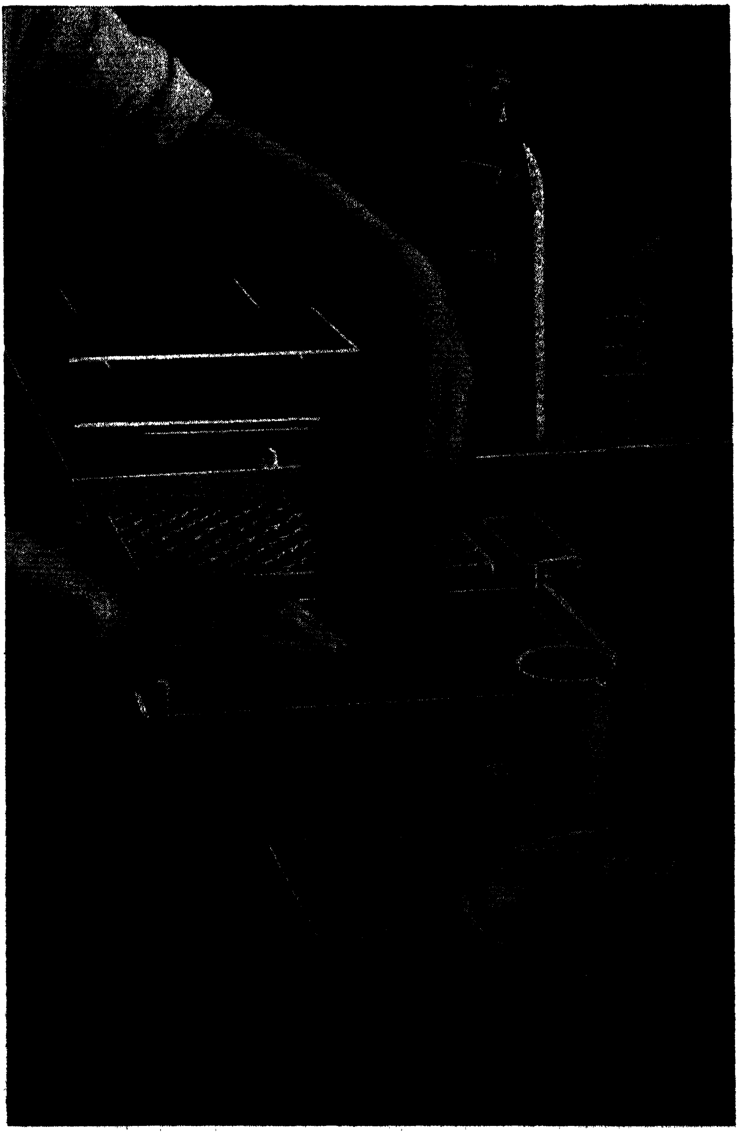
Formalin	750 gm.
Water	5,000 gm.

A recent British Patent, No. 519,164, 1940, of Gelaprint, S. A. Zurich, deals with improvements in the manufacture of bottle caps from gelatine compositions. In order to increase the elasticity and on account of the necessity to maintain the cap soft in the stored condition before use various resin emulsions (vinyl compounds and polyacrylic esters) are recommended for use in conjunction with the gelatine. The method of producing shaped articles consists of applying to a former a latex or a lacquer having a basis of an artificial resin, then drying the latex or lacquer, applying a liquid composition comprising gelatine, a softening agent and an artificial resin, partially drying the said coating, treating the gelatine layer with a hardening agent, applying a further coating of latex or lacquer having a synthetic resin base, drying the said coating and removing the shaped article from the former. The above type of cap is claimed by the inventor to be definitely superior to shrunk-on caps as it does not exhibit undesirable hygroscopicity.

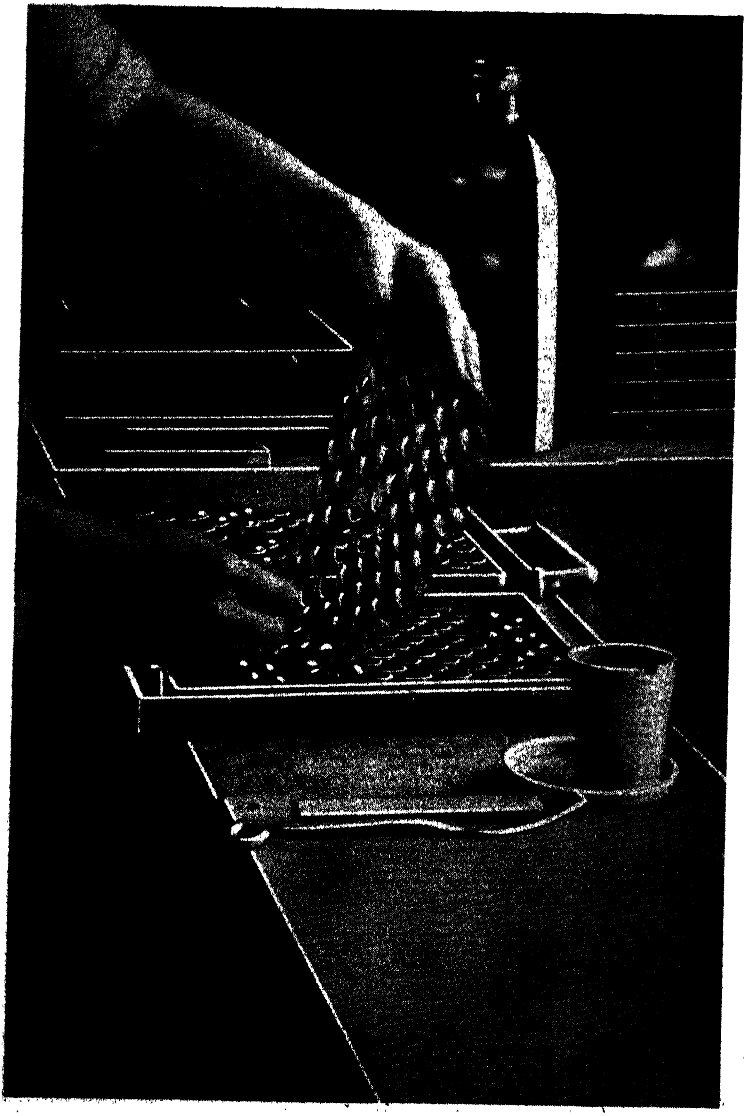
THE USE OF ISINGLASS IN BREWING

Isinglass is now used fairly extensively in the brewing industry in the form of what is technically known as "finings."

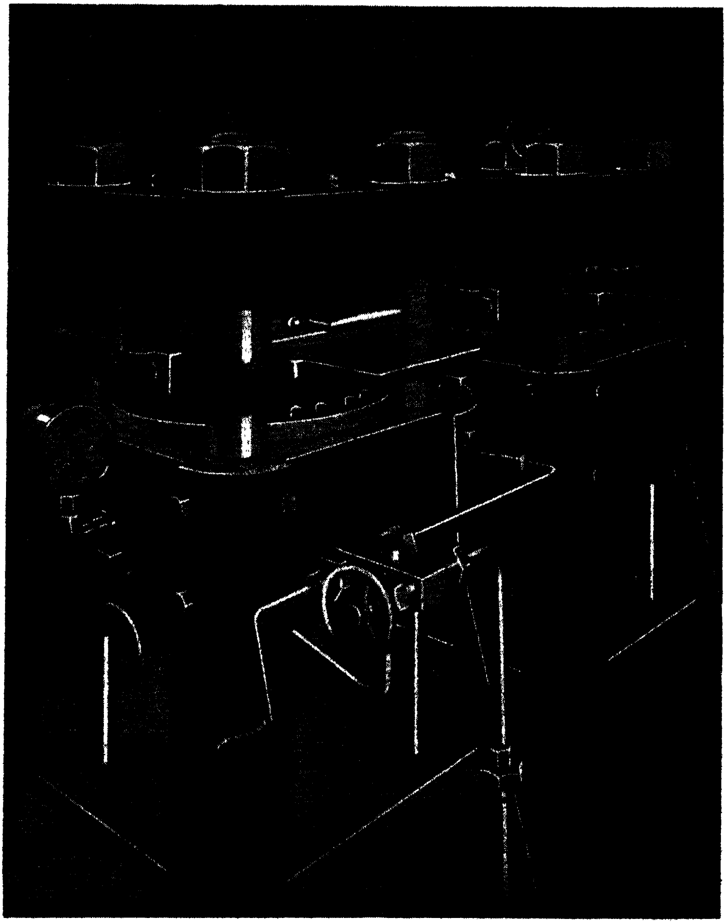
Finings may briefly be said to consist of solutions of isin-



First stage in the preparation of gelatine capsules.



Second stage in preparation of gelatine capsules.



Third stage in manufacture of gelatine capsules.

glass in tartaric or sulphurous acid, and are used to clarify beers. Their action is quite mechanical and depends upon the well-known coagulating property of isinglass, precipitating the suspended particles and brightening the product to a very appreciable degree. The use of finings is sometimes deplored by writers but provided the minimum amount is employed they cannot be regarded as objectionable adulterants. Generally speaking, a quart, irrespective of strength or gelatine content, is the amount used per barrel. The volume of beer displaced by the "finings" may be looked upon as a definite saving.

Only the very best quality gelatine is used in the preparation of "finings," preferably "Penang." Other well-known varieties are "Leaf Glass" and "Pipe Glass." The former is a thin transparent variety, whilst the latter is about three times as thick.

Tartaric, sulphurous, acetic and lactic acids are all used to dissolve the isinglass. J. Ross Mackenzie, in his manual, Brewing and Malting, writes:

> The first-mentioned acids—tartaric and sulphurous—have each of them their defects as "cutting agents." The former, though yielding an effective finings, encourages the development of mildew; the latter, though protective against mildew, produces a much less effective finings. Isinglass "cut" with tartaric, to which a proportion of sulphuric acid is afterwards added, yields finings, the power of which is not much lessened, while its resistance to mildew is sufficient for all practical purposes.

It has been found that beyond a certain concentration (.7 to 1.0 per cent H_2SO_3) the effective cutting increases in inverse ratio to the strength of the acid. Thus, undiluted commercial acid (7.4 per cent H_2SO_3) cut very slowly, and gave a very thin solution. At the commencement of the reaction (cutting) 1 per cent acidity (1 gal. of commercial acid per barrel), and at the close .2 per cent are good and workable strengths.

One gallon of commercial sulphurous acid (7.4 per cent H_2SO_3) is diluted with 6 gal. of water at first, and made up eventually to 36 gal. The amount of isinglass utilised by the brewer varies according to the quality, but the writers of the paper recommended 2¾ of best Russian or 3½ of inferior kind.

Another useful recipe is:

To 7 lb. of good isinglass, covered with water, add 1 lb. of tartaric acid, dissolved in warm water, and 1 to 1½ gal. of H_2SO_3, the latter added in small portions at intervals. Add fresh water as the isinglass swells. Rub through coarse and fine sieves, with intervals between each rubbing. Make up to 72 gal.

The cutting of isinglass is a very difficult and lengthy operation, and takes anything from a month to six weeks or more. Usually, a series of large tubs, hogsheads, is employed. The isinglass, swollen, of course, to a very appreciable degree, is sieved through the coarsest sieve first, and the finer ones in succession. Generally a mechanical action afforded by revolving brushes in the sieve, facilitates the passage through the interstices, and reduces the isinglass to a very fine state of suspension in the water.

British Patent 521,142, taken out by A. H. Gillman in 1940, deals with an improvement in the preparation of brewer's finings. The patent specification states that hitherto the preparation of finings has required a considerable length of time depending upon the size of the pieces of isinglass to be dissolved. Where the isinglass is cut into strips it takes as long as 4 to 5 days for the material to dissolve in tartaric and sulphurous acids and water. This involves the use of a number of large vats to store the materials during this time. To accelerate the process it is suggested by the patentee that the isinglass should be cut into fine threads and with continuous agitation the preparation of the solution reduced to 24 to 30 hours. The above invention covers the grinding of the isinglass to a fine powder and mixing with dry tartaric acid sulphites.

F. Prollius (Dingler's Polyt. J., CCXLIX, page 425) gives the following table of foreign samples of isinglass. (For the viscosity, one part of the specimen was dissolved in twenty parts of water.)

	Water, Per Cent	*Ash, Per Cent*	*Insoluble Matter, Per Cent*	*Time Required for Solution to Run Out, Seconds*
Astrakhan, from Schmidt and Dihlmann, Stuttgart	16.0	0.20	2.8	507
Astrakhan, from a collection	18.0	0.37	0.7	485
Astrakhan, fine iridescent Russian quality, Tubingen collection	17.0	1.20	1.0	500
Astrakhan, Russian, from Gehe of Dresden	19.0	0.80	3.0	491
Astrakhan, in laminal from Gehe	19.0	0.50	0.4	480
Astrakhan, in threads known as Hamburg threads	17.0	0.40	1.3	477
Hamburg isinglass	19.0	1.30	2.3	470
Another quality	19.0	0.13	5.2	. . .
Rolled Northern, fish bladder	1.5	3.20	10.8	467
Icelandish bladder	17.0	0.60	21.6	463
Indian isinglass	18.0	0.78	8.6	437
Yellow, quality unknown	17.0	2.30	15.6	360

Rideal, in his Glue and Gelatine Testing, mentions some substitutes for isinglass, thus:

Isinglassine made from calves' feet and other sources and reduced by machinery to a pliable homogenous mass, rolled out into sheets, dried, pressed, and shredded; each round is cut into about 125,000 shreds or staples.

Other substitutes are Irish Moss and Chinese Moss, both of which are of vegetable origin, and do not concern us at the moment.

The hydrogen-ion concentration of the beer affects the "fining" to an appreciable degree. It is suggested that a pH somewhere near the isoelectric point of isinglass is the best figure. Beer of too great an acidity refuses to take finings.

THE USES OF GELATINE IN BACTERIOLOGY

The finest leaf gelatine is used in bacteriology for the preparation of nutrient gelatine media.

In this case, the gelatine must be perfectly free from all micro-organisms; this is most essential. The presence of foreign bacteria in the gelatine will complicate the whole process of growth of the particular organisms under observation. Unreliable data may be obtained in this manner.

Air bubbles and the presence of string fibre can be more or less overlooked whilst sulphites and phenolic additives, etc., are extremely detrimental to free growth of organisms.

Where gelatine is used for plating out, then the presence of antiseptic bodies has a tendency to cause the colonies to become huddled together, instead of spreading out over the entire surface.

Color is also important. The formation of pigments is one of the chief indications that a certain type of organism is present. If the color is masked by the prevalent dark hue of the gelatine, then the test cannot be carried out with any degree of accuracy.

Some manufacturers add sugar and glycerine to their gelatine products, in order to improve its physical properties, although it has been shown that there is no such improvement. The presence of these substances in gelatine to be used for bacteriological research may quite possibly result in fermentation taking place during growth of the organisms.

From the above notes it should be evident that the gelatine used in bacteriology must necessarily be of the finest possible quality.

Gelatine favors the growth of a comparatively large number of organisms, but there are some types which have a decided liquefying effect, and so cannot be cultivated in this media. In order to ascertain the gelatine liquefying properties of an organism, it is usual to make what is commonly known as "stab culture."

A test tube is half filled with sterile gelatine solution, and the latter allowed to cool to form a firm jelly. The surface of the gelatine is then pierced by means of a platinum wire contaminated with the bacteria to be tested. Some organisms liquefy the gelatine in a few hours, while others take days or weeks.

Any modern work on bacteriology will give full details regarding the preparation of a nutrient gelatine medium and it is, therefore, unnecessary to recapitulate. The following precautions should, however, be taken by the bacteriologist:

1. Use of chemicals of the highest degree of purity, i.e., pharmaceutical quality.
2. Meat should be fresh lean bone.
3. Peptones, dry, made from meat.
4. Glycerine re-distilled.
5. Agar-agar, finest grade of commercial agar.
6. Photographic quality gelatine washed as free as possible of acid and impurities.

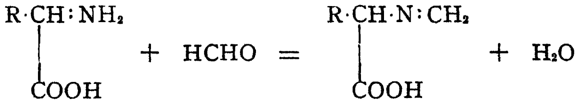
THE USES OF GELATINE IN CHEMICAL ANALYSIS

Gelatine finds some use in chemical analysis. An important application in applied research is in the examination of enzyme bates and similar preparations used in the leather industries.

As it is well known, enzyme bates depend for their main action on the common proteolytic enzymes.

Pickard (Jour. Soc. Leath. Trades Chem., Sept., 1924) mentions the following methods for the measurement of proteolysis:

1. The casein substrate method. Based on the solubility of pure casein in alkali, and its precipitation method. After complete proteolysis, the casein is not precipitated.
2. The gelatine substrate method. Based upon the relative setting power of the gelatine solutions before and after proteolysis.
3. The fibrin substrate method. Generally arranged colorimetrically by the liberation of a suitable dye from fibrin.
4. The Formal method (Sorensen). A titration method after proteolysis of a suitable protein. Amino acids are formed, which, after the addition of pure formaldehyde, are converted into methylene derivatives.



$$\begin{array}{l} R\cdot CH{:}NH_2 \\ | \\ COOH \end{array} + HCHO = \begin{array}{l} R\cdot CH\cdot N{:}CH_2 \\ | \\ COOH \end{array} + H_2O$$

The late Mr. J. T. Wood, undoubtedly the greatest authority on the mechanism of enzyme bates, was in favor of the gelatine method of proteolysis, following the rules laid down by Fermi (Wood and Law, J. Soc. Chem. Ind., 1912, page 1108).

In referring to the effect of enzymes on the substrate, Pickard writes:

The use of different substrates may lead to widely different results unless the relationship between enzyme and substrate is logically considered. Bile salts for example, show no activation of trypsin when the latter is tested in a gelatine substrate, but if a fatty casein be used as a substrate, the trypsin is better able to hydrolyse the casein owing to the fat-removing action of the bile salts, and the consequent exposure of the real substrate (casein) to enzyme activity.

Northrop (J. Gen. Physiol. Chem., 1919, page 216) finds "the rate of hydrolysis of gelatine and casein to be constant when the concentration of the latter reaches 3 per cent."

Bogue points out that Grete (A. Grete, Ber., *21* (1888), *2762*; *32* (1909), 3106) has used gelatine in the volumetric estimation of phosphorus as phosphate. In his own words he finds:

> An addition of gelatine, or similar substance as peptone, results in a precipitate of phosphomolybdate that is whitish and voluminous, such that a very small amount of phosphoric anhydride, e.g. 0.000125 gm., will reveal itself as a distinct cloud in the clear liquid. By a short warming, the gelatine separates from the phosphomolybdate and the precipitate assumes the usual yellow compact form and settles readily and quickly. Upon a further addition of a little molybdic acid solution, so long as any phosphoric acid remains, a voluminous gelatine, containing precipitate, will again come down. It is possible by this means, through continued additions of molybdic acid and subsequent heating and settling of the precipitate, to titrate to a sharp end point.

THE USES OF GELATINE IN THE LEATHER INDUSTRY

Gelatine is much used in leather manufacture as a finish, although it is not so well suited for this purpose as others of the mucilages.

Flemming (Practical Tanning) gives the following recipe for a "Bright Blacking Varnish for Shoe Leathers":

For use, dissolve 2 oz. of gelatine (isinglass) by boiling in 1 qt. of water. To this solution add 1 oz. of indigo blue and 2 qt. of cold water. Let the solution cool, and place it so as to be able to see that the mixture is not too thick, as the heat of the shop or summer weather has much to do with the amount of water the gelatine will absorb. The mixture should be like thin jelly. It is prepared by heating the gelatine a little and straining through cheese-cloth; then mix equal parts of alcohol, gum, and gelatine, and stir until the mixture gets thick. While stirring, add to each gallon of the mixture 1½ oz. of glycerine. When well set, the mixture is ready to be applied to the leather.

Two thin coats should be evenly spread on the grain with a sponge and well rubbed in with a fine sponge or with a soft hairbrush in a warm room.

Let the first coat get dried in before applying the second. After the last coat is absorbed, glaze the leather slightly by hand so as to produce the soft feel the stock had before the varnish was applied. If these instructions are carried out, the leather will have a pleasing finish.

High grade gelatine is used in the finishing of hat leathers. It is important that the gelatine used for this purpose should be free from iron and other mineral impurities likely to discolor the band. Lamb suggests that the following facts should be taken into account when considering the preparation of a gelatine mucilage:

> The best form in which to apply either glue or gelatine is as a thin, soup-like mucilage. It is impossible to give quantities, as these depend entirely upon the solidifying power of the particular glue or gelatine that is being used. Very often a 1 per cent solution of gelatine of fair quality makes a much stronger mucilage than a 4 or 5 per cent solution of a common quality glue. That is to say, 1 lb. of gelatine is in many cases equal to 4 or 5 lbs. of glue, so that it often pays to buy a good quality gelatine rather than a common quality glue.

A very common use for gelatine is as a bottom before staining, especially for common leathers, where the grain is poor and needs adequate covering. Again, the gelatine prevents the dye from sinking right into the center of the leather and causing uneven results.

Lamb (Leather Dressing) mentions that gelatine or glue rendered insoluble by the action of formaldehyde makes an excellent waterproof finish for hat leathers, upholstery and bookbindings:

> To 100 parts of a 2 per cent solution of a gelatine of good quality 5 parts of a 40 per cent solution of formaldehyde are added, and a light coat of this season is given to the leather; the leather being then dried in a fairly warm stove, in order to drive off the excess of formaldehyde. Only sufficient of the finish for the requirements at the time of making it should be prepared, for the reason that during a long standing the formaldehyde is steadily acting upon the glue and making it insoluble, so that when the mixture has become set, it is impossible to remelt it again. If desired, the gelatine solution may be applied first to the leather, afterwards making the application of formaldehyde. The leather should be finally dried at a moderately high temperature.

In conclusion, it should be pointed out that whenever possible the same make of gelatine should be used, and thus the same quantity can always be employed, this making for uniform results. The glue pot must on no account be allowed to become foul, otherwise intensive hydrolysis will take place, causing the glue to lose much of its adhesiveness. Every possible care has to be taken to ensure absolute cleanliness, as the gelatine liquor forms an ideal media for the cultivation and rapid growth of gelatine-liquefying micro-organisms.

INDEX

A

Acidity of gelatine, 93
Acidulation of bone stock, grading and, 42
Additives, chemical, 67
Amino acids, 14, 15
Applications of glue as an adhesive, 99
Applications of glue, miscellaneous, 104
Ash content of photographic gelatine, reducing, 64
Atropine discs, 128

B

Bacterial count for edible gelatine, 93
Bacteriology, uses of gelatine in, 137
Boiling, 44
Bone fat, 52
Bone fat, recovery and purification of, 79
Bones, 30
Bones, degreasing, 48
Bones, extraction of, 47
Bone stock, grading and acidulation of, 42
Brewing, use of isinglass in, 130

C

Calfskin, 25
Chemical additives, 67
Chemical analysis, uses of gelatine in, 139
Chemical composition of gelatine and collagen, 17
Chemicals, addition of, 61
Chemistry of proteins, introduction to, 14
Chrome leather waste, glue from, 56
Clarification, 61
Clarification, decoloration and, 63
Cocaine discs, 129
Cod-haddock and catfish skins, glue from mixed, 55
Collagen, 14
Collagen, chemical composition of gelatine and, 17
Cooling, 75

D

Decoloration and clarification, 63
Degreasing bones, 48
Deliming, washing and, 42
Distinction between gluestock and gelatine stock, 32

E

Early history, 1
Evaluation of glue and gelatine, 90
Evaporation, 69
Extraction of bones, notes on the, 47
Extraction of fish waste, 54
Extraction of gelatine from gluestock, 44

F

Fibre structure of proteins, 6
Filtration, 61
Fish waste, 31
Fish waste, extraction of, 54

Foam gelatine, 77
Foodstuff industry, gelatine in the, 115
Furrier's waste, 29

G

Gelatine in bacteriology, uses of, 137
Gelatine capping, 129
Gelatine in chemical analysis, uses of, 139
Gelatine and collagen, chemical composition of, 17
Gelatine, extraction from gluestock, 44
Gelatine in the foodstuff industry, 115
Gelatine, influence of chemical agents on nature of, 9
Gelatine in the leather industry, uses of, 140
Gelatine in the manufacture of marshmallows, 121
Gelatine, miscellaneous applications of, 123
Gelatine in pharmacy, uses of, 123
Gelatine for the photographic industry, 107
Gelatine plant construction, plastics for, 95
Gelatine, properties of, 87
Gelatines, analysis of high grade British, 88
Gelatine stock, distinction between gluestock and, 32
Gelatine, tests for, 124
General methods of preserving stock practiced by the glue manufacturer, 35
Glue from chrome leather waste, 56
Glue and gelatine, evaluation of, 90
Glue joints, tests for the strength of, 104
Glue, miscellaneous applications of, 104
Glue from mixed cod-haddock and catfish skins, 55
Glue, properties of, 86
Gluestock and gelatine stock, distinction between, 32
Gluestock, preservation of, 35
Gluing conditions and procedure, 100
Glycerine jelly, 126
Goatskins, 28
Grading and acidulation of bone stock, 42
Green and salted stock, washing of, 37

H

Heat conductivity, relative, 71
Hide offal, 27
Hide proteins, hydrolysis of, 17
Hide and skin offal, 22
Histology of skin, 4
Hydrolysis of hide proteins, 17

I

Ice cream as influenced by gelatine, physical properties of, 118
Ichthamol paste, 127
Isinglass in brewing, the use of, 130
Isinglass raw materials, 33

K

Keratin, structure of, 7

L

Leather industry, uses of gelatine in, 140
Leather scrap, 30
Liming, 40

M

Marshmallows, gelatine in the manufacture of, 121
Miscellaneous applications of gelatine, 123
Multiple evaporation, 73

O

Offal, hide, 27
Offal, hide and skin, 22

P

Pharmacy, uses of gelatine in, 123
pH of gelatine, 93
Photographic gelatine, reducing ash content of, 64
Photographic industry, gelatine for, 107
Photo-lithography, 112
Physical properties of ice cream as influenced by gelatine, 118
Pigskin, 28
Plastics for gelatine plant construction, 95
Preserving stock, general methods of, 35
Procedure and conditions of gluing, 100
Proteins, fibre structure of, 6
Proteins, hydrolysis of hide, 17
Proteins, introduction to chemistry of, 14
Purification of bone fat, 82

R

Raw material for glue and gelatine, 21
Raw materials for isinglass, 33
Reducing ash content of photographic gelatine, 64
Relative heat conductivity, 71

S

Salted stock, washing of green and, 37
Scrap, leather, 30
Sheepskins, waste from, 27
Skin greases, 83
Skin greases, recovery and purification of, 79
Skin, histology of, 4
Skin proteins, effect of chemical agents on, 9
Strength of glue joints, tests for, 104

T

Tankage after extraction of gelatine, 60
Tankage greases, 84
Tests for gelatine, 124
Tests for the strength of glue joints, 104

U

Use of isinglass in brewing, 130
Uses of gelatine in leather industry, 140
Uses of gelatine in pharmacy, 123

W

Washing and deliming, 42
Washing of green and salted stock, 37
Washing, liming and deliming of gluestock, 35
Waste, fish, 31
Waste, furrier's, 29
Waste from sheepskins, 27
Waterproof paper, 130

Z

Zinc jelly, 127, 128