The Products of the Destructive Distillation of Keratin in the Form of Leather

by R. Phillips Rose

1913

Submitted to the Department of Chemistry of the University of Kansas in partial fulfillment of the requirements for the Degree of Master of Science

THE
DESTRUCTIVE DISTILLATION
OF KERATIN

R PHILLIPS ROSE

1913

THE PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF KERATIN IN THE FORM OF LEATHER.

By

R. Phillips Rose

Presented to the Faculty

of the

GRADUATE SCHOOL

of the

University of Kansas

In Partial Fulfillment of the Requirements

for the degree of

MASTER OF SCIENCE

May 15, 1913.

INTRODUCTION.

This research was undertaken for the purpose of finding a method for the commercial utilization of leather scrap from boot factories. (It was done in the Department of Industrial Research of the University of Kansas, under the direction of Dr. Robert Kennedy Duncan). The work will be considered from a theoretical and practical point. Since the commercial application would simply be the application of engineering principles, to the known scientific facts obtained.

In the classification of chemical substances, leather comes under the general caption of protein compounds. According to Mann[1], protein substances may be divided into three groups:

1. Albumins occurring as "native albumins".

They include the albuminoid substances

which form the supporting and connective tissue of the animal organism.

2. Proteins or "Proteids" proper, which are combinations of albumins proper with other organic compounds, containing phosphorus or iron.

3. Derivatives of native albumins and proteins which retain in their chemical configuration the characteristics of albuminus substances, as represented by albumins, peptones, peptides as products of digestion or metabolism, either natural or artificial.

The decomposition products of the above compounds have been a subject of investigation which early attracted the attention of chemists. It was early recognized, that on account of the complexity of the albumin molecule, the only methods that would ultimately lead to its structural formula would be a study of the products obtained

----

1. "Chemistry of Proteids", P. 4, First Edition.

from its decomposition by various methods. From
the knowledge thus obtained, it was hoped that the
original compounds could be synthesized, and in
fact much success along this line has been gained
by Emil Fischer of Berlin and his pupils. While
no albumin, which could be identified as "native"
has as yet been obtained, still complex poly-pep-
tides, as Fischer terms them, giving practically
all of the special reactions characteristic of al-
buminous substances, have been synthesized. One
aim of the various processes used was to preserve
the original chain intact, breaking only the imid
linking (which linked together the side chains),
so that its linking could be identified. The
products that result when this reaction takes
place are called the primary dissociation products,
while those in which the chain is ruptured, are
called the secondary dissociation products. In
the secondary decomposition, the same products
are obtained in general as in the primary decom-

position, but a part of the compounds break down into simpler products. This fact applies to the three classes of albuminous substances noted above. The products of both the primary and secondary decomposition are in general the same for the classes, with the exception of a very few of the minor individuals of each class. There is a wide variation in the ration of the amounts produced for each class and for each individual in the class.

The primary dissociation products of albuminous materials are obtained by fermentation or hydrolysis with acids. Acid hydrolysis is considered equivalent to the action of ferments. One of the more common methods is that of Hlasiwetz and Habermann.[1] These experimenters boil the albumin in a solution of hydrochloric acid containing stannous chloride. This reaction breaks the imid grouping (by means of which the chains are kept together) without breaking the chain itself, that

1. Liebig's Ann. 159, 204, (1871).

is without changing the relative position of the nitrogen atoms. One proof of this is shown by Schylze[1], who showed the changes which took place in guanidin, when treated by the above, to be as follows:

-CO-NH-CNH-NH-C- becomes COOH-NH-CNH-NH-C

Without going into the details of the isolation and estimation of the primary decomposition products, the following list is given according to Cohnheim.

A. OPEN-CHAIN AMINO-ACIDS.

1. (a) mono-amino-mono-carboxylic acids
    1.   amino-acetic $C_2H_5NO_2$
    2.   amino-propionic $C_3H_7NO_2$
          amino-butyric $C_4H_9NO_2$
    3.   amino-valerianic $C_5H_{11}NO_2$
    4.   amino-iso-butyl-acetic $C_6H_{13}NO_2$
   (b) mono-amino-mono-carboxylic-hydroxy acids
    5.   amino-hydroxy-propionic $C_3H_7NO_3$
    6.   amino-tetra-hydroxy-caproic $C_6H_{13}NO_6$
   (c) mono-amino-di-carboxylic acids
    7.   amino-succinic $C_4H_7NO_4$
    8.   amino-glutaminic $C_5H_9NO_4$
   (d) mono-amino-di-carboxylic-hydroxy acids
    9.   amino-hydroxy-succinic $C_4H_7NO_5$
    10.   amino-hydroxy-suberic $C_8H_{15}NO_5$

[1]. Liebig's Ann. 169, 150 (1879).

A. OPEN-CHAIN AMINO-ACIDS. (cont.)

    II. (e) diamino-mono-carboxylic acids
        11.   diamino-propionic $C_3H_8NO_2$
        12.   diamino-caproic $C_6H_{14}N_2O_2$
        13.   guanidin-amino-valerianic $C_6H_{14}N_4O_2$
        14.   histidin $C_6H_9N_3O_2$
   (f) diamino-mono-carboxylic-hydroxy acids.
        15.   diamino-trihydroxy-dodecanoic
   (g) diamino-di-carboxylic acids
        16.   diamino-glutaric $C_5H_{12}N_2O_4$
        17.   diamino-adipic $C_6H_{14}N_2O_4$
   (h) diamino-di-carboxylic-hydroxy acids
        18.   diamino-di-hydroxy-suberic $C_8H_{16}N_2O_6$
        19.   diamino-hydroxy-sebacic $C_{10}H_{20}N_2O_5$
        20.   caseanic acid (?) $C_9H_{16}N_2O_6$
        21.   caseinic acid (?) $C_{12}H_{16}N_2O_5$

B. RING-COMPOUNDS. (See Histidin under No.14)

    (i) pyrrolidin compounds
        22.   a-pyrrolidin-carboxylic acid $C_5H_9NO_2$
        23.   hydroxy-pyrrolidin-carboxylic
                           acid $C_5H_9NO_3$
    (k) aromatic amino-acids
        24.   phenyl-amino-propionic $C_9H_{11}NO_2$
        25.   phenyl-hydroxy-amino-propionic $C_9H_{11}NO_3$
        26.   indol-amino-propionic $C_{11}H_{12}N_2O_2$

C. AMMONIA.

    (l) ammonia

        27.   ammonia NH_3

D. THIO-AMINO-ACIDS.

    (m) diamino-di-thio-dicarboxylic acid

        28.   cystin $C_6H_{12}N_2O_4S_2$

Since in the experimental work we are dealing only with keratin, a discussion of the above products will not be taken up at this time, but those which are derived from keratin will be considered under that heading.

The secondary dissociation products are those resulting from the action of reagents upon the primary products. The most common reagents used to produce this class of compounds are boiling alkalies, superheated steam, oxidizing reagents, such as calcium, barium and potassium permanganates in boiling acid or alkaline solution, hydrogen peroxide in acid solution, fusion with alkalies and dry distillation. The action of these reagents upon the complex proteins produce a great number of simpler products included in all the divisions of organic chemistry and are too numerous for tabulation in a paper of this kind.

Animal hides are made into leather, which is composed principally of the albuminoid keratin combined either chemically or coloidally with some other substance, the principal ones of which are tannin and chromic oxide. Tannin is one of the most common precipitants for albuminous solutions and is supposed by many chemists to form a compound with the albumin; others believe it to be a coagulation of the albumin, which carries down most of the tannin. Many examples of this class of reaction are known in colloidal chemistry and it is also a fact that the solutions of albuminous substances are, for the most part, colloidal in their nature. Chromic acid is another important coagulating reagent and it is by the reduction of chromic acid to chromic oxide in the raw skins that leather is produced.

It is a well known fact that all animal tissues are made up of cells which are capable of being

differentiated only under the microscope. Leather, when examined under the microscope shows a fibrous structure. From these considerations it is perfectly obvious that the cells of the hide, when in the swelled and semi-colloidal condition brought about by the usual tan house treatment, could be conceived as being coagulated into fibers by the tanning material which is absorbed in great quantities by the cells during coagulation. The subsequent rubbing and oiling which the hide undergoes after the tanning proper, serves further to complete the action, and where oil or leather dressing is used to form around the fibers a protective coating. A well known fact supporting this argument is the coagulation of blood - first into a gelatinous mass and then into fibers.

From the above considerations, it seems reasonable to conclude that the decomposition product of leather will be ultimately the same as those of the

albuminoid keratin when both are treated under the same conditions. From our knowledge of the destructive distillation of organic substances, the most common of which are coal, wood, bones, peat and lignite, it is reasonable to conclude also that the destructive distillation of keratin in the form of leather will yield a coke or charcoal containing the mineral constituents of the original substance and reduced carbon, a liquid distillate containing the moisture originally in the leather, and the decomposition products of the keratin both primary and secondary, and lastly a gas containing the volatile constituents of the decomposition products, together with carbon monoxide and dioxide formed from the hot decomposition products and the oxygen of the air.

Since this research was conducted in order to obtain a commercial method for the utilization of leather scrap, the charcoal residue, the nitrogen content of the distillate and the utilization of

the gas as fuel, are the factors considered at greater length in this paper.

APPARATUS.

The apparatus used in the preliminary experimental work for this paper consisted of a cast iron retort twenty-five centimeters high and fifteen centimeters in diameter. This retort was fitted with an iron cover bearing an exit tube, which leads to a common Liebig condenser and a thermometer tube. The cover was secured to the retort by means of clamps, the whole being made gas tight by means of an asbestos gasket. The retort would contain from two to two hundred and fifty grams of leather scrap. The heating was carried out by means of a ring gas burner.

The heating by the gas burner was very unsatisfactory on account of the unequal temperature. It was a common occurrence to have the lower part of the retort a cherry red which denoted a temperature of 600^{0} to 700^{0} C., while

the thermometer which extended to the center of the charge registered about 300° C. On this account and the smallness in capacity of the retort, a new one was designed and constructed. It consisted of a cast iron cylinder forty centimeters in heighth and twenty-five centimeters in diameter. These are inside measurements. The retort was fitted with a flange to which was bolted the cover by means of eight three-eighth inch machine screws, the whole being made gas tight by means of a carefully ground joint. The sides and bottom of the apparatus were one and half^{a} centimeters in thickness, the outer part of the cover was of the same thickness, but inside the ground joint it was a half centimeter thicker.

The cover was fitted with a three quarter inch iron pipe which lead to a worm condenser made by enclosing a turn and a half of three quarter

inch pipe, the diameter of the circle being thirty five centimeters, in a copper cooling vessel. The exit pipe of the condenser lead to a receiver consisting of a large glass bottle. The retort was also fitted with a thermometer tube inserted midway up the side and extending into the center of the retort.

The heating was carried out by means of an electric heater composed of forty-five feet of nichrome resistance wire, with a resistance of eleven ohms, wound uniformly on the retort. This wire carried ten amperes on a one hundred and ten volt circuit. This current produced a temperature of 420° C. in five hours. In order to cut down radiation the retort was placed in a galvanized iron can twenty centimeters larger than the retort both in heighth and diameter. A layer about twelve centimeters in thickness of double float-

ed silica was packed in the bottom of the can, the
retort placed in and the silica packed around it to
the top.   The thermometer tube was extended through
the outer wall.   After the charge was placed in the
retort and the cover put in place, asbestos fiber
was packed over the top.   This method of heat insula-
tion gave very excellent results and its efficiency
can be seen from Table I.

Table I

Showing the Efficiency of the Electric
Coil for Heating the Retort.

Time hrs.	Temp.	Dif.
0	35	---
1	110	75
2	176	66
3	237	51
4	285	48
5	355	40

The retort was capable of carrying a charge of fif-
teen to sixteen hundred grams of leather scrap.

The outlet tube from the glass receiver lead
to an ordinary filter pump where the obnoxious
gases were mixed with water and run into the sewer.

EXPERIMENTAL.

As noted in the introduction, from what is known of the decomposition of organic compounds, it is to be expected that keratin in any form will break down into a distillate containing the moisture in the keratin together with the liquid and solid products of decomposition, a gas containing the volatile products of the decomposition, carbon dioxide and monoxde formed from the residue and the air in the retort, and a residue remaining behind containing the mineral constituents used in the tanning process and a quantity of carbon.

It was flound that, by heating the small retort and contents for five hours by means of the ring burner a yield of 48 to 50 per cent charcoal was obtained when the temperature was not raised above 300° in the center of the charge. With increased temperature the yield of charcoal decreased to

32 per cent of the original weight. In every case
the heating was continued until no more liquid dis-
tillate was obtained and until the evolved gases were
colorless. It was found that this required approx-
imately five hours with the gas heated retort and
eight hours with the electrically heated retort. The
yield of charcoal from the electrically heated retort
varied in the same way as did the gas heated one.
It was found that upon letting the temperature raise
gradually,as indicated in Plate I, until it had
reached 420° C., and then shutting off the current,
the retort cooling down gradually, that a yield of
48 to 50 per cent charcoal invariably resulted.

The amount of distillate obtained varied considerably with the conditions. When the gas heated retort was used, an average yield of 28 per cent by weight of distillate was obtained; the yield varied from 24 per cent for rapid heating to 31 per cent for slow heating. The distillate divided itself into two portions, one containing the aqueous part and the other made up of an oil or tarry layer. The oil portion varied in the same way as the percentage yield of distillate, that is, when the heating was rapid the percentage of oil would be very low and when slow it would be high. It was found that by passing the evolved vapors through a second retort heated red hot that the oil could be made to disappear altogether.

The yield of distillate with the electrically heated retort was always higher than for the gas

heated one.   The following table shows yields of
charcoal and distillate from five runs:

	Charcoal Per cent	Distillate Per cent
No. 1.	52.0	33.8
2.	51.0	35.0
3.	51.5	34.0
4.	51.0	35.5
5.	51.0	34.9

These results show an average loss of 14 per
cent.   The loss was mostly of a gas. This gas had
an extremely nausating odor.

The research may be considered under the
three following divisions; first, investigation
of the carbon residue;   second, of the distillate
and third of the gas.

By the term charcoal is understood the car-
bon residue resulting from the distillation. This
brings up the question as to what are the char-
acteristic properties of the two carbon residues

obtained from the decomposition of carbonaceous materials, termed coke and charcoal. Some authorities use the term coke for the carbon residue from coal and call all others charcoal while others use the term charcoal to designate the residue from all organic material of animal and direct vegetable origin. It does not seem that either one of these uses are correct and a better differentiation is possible by looking at the structure of the residue itself defining those which **melt or sinter** together and are made porous by the gases escaping through the semi-molten mass, cokes, and those in which the material does not sinter together but in which the original structure is somewhat preserved, charcoal. According to this differentiation, the residue from the destructive distillation of keratin in the form of leather would be a charcoal, for its original structure is in some measure preserved and in no case has sintering occurred.

Since, as shown in the introduction, the decomposition products of all albuminous materials are principally nitrogenous compounds, the nitrogen content of the different portions of the products are more or less a criterion of the completeness of the reaction. Therefore, analyses of several of the charcoals obtained were made by the Kjehdahl method. Results were obtained showing a nitrogen content of from 4.5 to 8 per cent, and the variation was found to depend on the heating, the more gradual the heating the smaller the percentage of nitrogen remaining in the residue. These results are substantiated by the work of Mond[1], and more recently by Dr. J. W. Parr[2] of the University of Illinois.

The percentage of carbon in the residue is very high in comparison with the other commercial charcoals, namely, bone charcoal. The results

[1]. J. Soc. Chem. Ind. 1889.
[2]. Communication on unpublished work.

of several analyses are as follows:

Table I.

Ash Content of Charcoal.

6

Source	No. I % Ash	No.II % Ash
Vegetable tanned leather.....	4.815	4.799
Mineral tanned leather.......	13.256	13.261
Commercial bone black	87.000	87.050
Commercial bone black	83.370	83.400
Commercial bone black	82.46	82.440
Kahlbaum's Acid Purified bone black	1.746	1.783

In every case the estimation was made by ignit-
ing the charcoal to constant weight in porcelain
crucibles heated in an electric muffle.

The analysis of the various ashes showed the
following results: the ash from the mineral tan-
ned leather consisted principally of chromic
oxide, together with a trace of calcium sulphate
and sodium chloride and sulphate, the ash from

the bone black consisted principally of calcium
phosphate, with traces of sodium sulphate and
chloride.

The commercial uses of charcoals depend prin-
cipally upon their power to absorb coloring matter
our of solutions such as sugar and oil; and on
account of the insight which absorption tests
would give as to comparative absorption powers
of the structure of the charcoal, quite a lot of
work has been done on this phase of the subject,
but since it has no direct bearing on the sub-
ject of this paper, it will be discussed only
very briefly.

During the past few years the attention of
chemists and physicists have been directed to the
subject of the absorption of substances in sol-
ution by other substances such as charcoal and
the hydrogels of many colloidal substances.

The work of Van Bemmelen on the absorption by
hydrogels, of Ramsay on the absorption of gases
by charcoals and of Freundlich on the swelling
power of hydrogels has proven that absorption is
a surface phenomenon and that the substances that
are absorbed best from solutions are those which
concentrate in the surface film of the solution.
Recent original articles have sought to show that
the clarification of sugar solutions by bone char-
coal depended upon the amount of the nitrogen
content, and by others upon the calcium phosphate
content. These papers indicate that, as long as
there is no reaction between the mineral consti-
tuent of the charcoal and the substance in solu-
tion, the absorption of the substance from the
solution is not affected by the mineral consti-
tuent. The only part possible for the mineral
constituents to play is to effect a change in
the structure of the charcoal during such treat-

ment as revivifying.

Several series of comparative absorption
tests were made upon the leather charcoal and
commercial bone black, using solutions of com-
pounds that were known to concentrate in the sur-
face film such as iodine, certain salts and or-
ganic dyes.   The manipulation was very simple;
the charcoals were ground to the same size mesh,
weighed out in 1 gram lots, placed in 500 c.c.
Jena Erlenmeyer flasks and heated under reduced
pressure for a short time.   After cooling the
solutions were run in.   Every precaution was
taken to keep the conditions equal for all the
determinations in each series.   It was found
that if the preliminary heating was not carried
out, no duplication of results could be obtained.
This was presumably on account of the absorbed gases,
which escaped in large quantities from all the
charcoals, upon heating.

Since the results for all of the solutions run in the same ratio, only one series using an iodine solution will be given. The analyses for iodine were made with standard sodium thiosulphate in the usual way.

The charcoals used were ground to 30-50 mesh and treated as described above:

Time of absorption Charcoal used	No. I 12 hrs	No. II 24 hrs	No. III 36 hrs.	No. IV 60 hrs.
Mineral tan	62.97	81.52	95.11	98.28
Vegetable tann	25.55	44.68	63.45	83.40
Bone black	18.42	36.71	51.24	65.00

The results show that the leather charcoals are superior in absorbing power to the bone charcoal. It is very probable that the great superiority of the charcoal from mineral tanned leather is due to the structure being preserved to a greater extent than in the vegetable tanned by the presence of the chromium oxide.

The Distillate and Gases.

As mentioned above, the distillate divided
itself into two distinct parts, an oil layer and
an aqueous layer.   The aqueous portion smells
strongly of ammonia and slightly of pyridine.
By the use of a glass condenser, it was possible
to note the formation of the products to some
extent and six stages could be clearly differen-
tiated.   At first when the temperature had
reached about 160^0 C., a dense vapor, smelling
strongly of ammonia, was given off. These vapors
would not condense by simply cooling, but were,
for the most part, readily soluble in water and
acids. Next came a white opaque liquid, rather
viscous in appearance, and as is the case with
many organic compounds, it turned brown on expos-

ure to the air.   After this came a white crystal-
line solid, fourth a reddish liquid, fifth a red-
dish crystalline compound and sixth the black oil
spoken of above.

A volume of the distillate, equaling about a
liter was collected and the two portions, oil and
aqueous separated from each other by means of a
separatory funnel.   The aqueous portion was sub-
jected to a steam distillation.   A small portion
of yellow liquid resulted, together with white
crystals which were identified as ammonium carbon-
ate.   A steam distillation of the oil portion re-
sulted only in a yield of the yellow oil.   This
compound upon standing turned dark.   A very small
quantity was obtained and its boiling point could
not be accurately determined, but lay between the
limits of 125^{0} and 140^{0} C.   With sulphuric acid it
gave a dark almost black precipitate.   This might
be taken to indicate pyrrol, C_4H_5N, since it boils

at 131° C., and gives with sulphuric acid a dark red brown precipitate.

The residues from the distillation of oil by steam was poured into a large graduated cylinder and allowed to separate into its two portions, the volume of oil was red. Dilute sulphuric acid was added and the content of the cylinder shaken thoroughly. The two liquids again separated and the volume of oil again read. No dimution of volume had occurred on washing. The aqueous portion was drawn off and the washing repeated, using dilute sodium hydroxide. The oil dissolved completely and readily in the hydroxide. It was also readily soluble in alcohol.

The tar was next analyzed for phenol, adcording to the method of Redman and Rhodes[1]. Only a trace was found corresponding to 0.7 per cent

[1] Jr.Ind.Eng.Chem., 4, 1912.

phenol calculated on the basis of the original
leather used. The tar, when dissolved in alcohol,
could be reduced to a light red solution by means
of zinc and hydrochloric acid. On the other hand,
oxidation, even when carried out in dilute solutions,
caused charring. On attempting to fractionate the
material the temperature rose to 200^0 C. and then
reduction started and the temperature fell rapidly.
The tar or oil constitutes from 3 to 4 per cent
of the weight of the leather used.

The aqueous portion of the distillate was
subjected to a fractional distillation and the re-
sulting fractions collected at ten degree intervals
from 30^0 to 110^0 C. These fractions were again
fractionated using a Zebel-Henniniger column with
the same result as before. These results perhaps

indicate that the boiling point of any compounds in
the volatile part of the distillate must be close
to that of water.

Many individual tests were made upon the dis-
tillate in order to find its various constituents.
Since we expected most of the constituents to be
nitrogenous in nature, the different class reactions
for the amines were tried. The distillate was test-
ed for primary amine. RNH_2 by the iso-nitril re-
action; that is, the formation of the characteristic
smelling iso-nitril from the amine by the action of
chloroform and alcoholic potash. In every case
this reaction gave negative results. A good test
for secondary amine R_2NH was obtained by converting
the base into nitrosoamine by means of nitrous and
then applying Libermann's reaction, namely, the
production of intensely colored solutions when
nitrosoamine is added to a solution of phenol in
concentrated sulphuric acid. On dilution these

solutions turn a deep blue or green. So far, how-
even, it has been **impossible** to isolate the base
which causes this reaction. It may be n-propyl
secondary amine, which has a boiling point of 98°
C., for as indicated above, the distillate boils
in the neighborhood of 100° C.

No results of any value were obtained from the
work on the composition of the distillate until an
adaptation of the methods for the separation of the
constituents of protein hydrolysis was discovered.
The distillate from 1500 grams of leather was col-
lected in sulphuric acid. Presumably no ammonia
escaped. This solution contained a large amount of
red brown powder which confirmed the observation
made above on the possibility of pyrrol. The sol-
ution was made up to two liters, separated from the
tar, and the precipitate filtered off; 500 c.c.
of this was evaporated to a syrupy condition.
Since ammonium sulphate was known to be present

the evaporation was continued until crystals began
to separate; 95 per cent alcohol was now added
until a precipitate appeared.   The mixture was
allowed to stand for about four hours. At the end
of that time the precipitate was filtered off dried
carefully and weighed. A yield of 12 per cent of
the weight of leather used was obtained. Analysis
for both ammonia and sulphuric acid in the precip-
itate gave 98.76 per cent pure ammonium sulphate.
This shows 2.87 per cent N. in the form of free
ammonia.

The filtrate from the above was concentrated
and made up to a definite volume, an aliquot kak
part taken and a determination of nitrogen made
by the Kjehdahl method. 3.47 per cent of the
weight of the leather, as nitrogen was found. This
represents the amount of nitrogen contained as mono-
and di- amino acids, together with the ammonium
sulphate, which was soluble in the alcohol used.

The remainder of the solution was now sep-
arated with barium hydroxide to free it from sul-
phuric acid and the remaining "easily replaceable"
nitrogen. The solution was filtered and a solution
of 10 per cent phospho-tungstic acid added. A
heavy precipitate came down. Phospho-tungstic acid
precipitates the diamino acids, arginin, guanidin-
a-amino-n-valerianis acid, lysin, a-e-diamino-n-
capric acid and histidine, whose composition has
not yet been determined. No method has as yet
been found for identifying the constituents of
this precipitate. They are easily soluble in
silute alkalies, but not in acids, except concen-
trated hydrochloric acid. The filtrate from the
phospho-tungstic acid precipitate was next con-
centrated until crystals began to separate. It
should contain the monoamino acids such as glycocoll,
leucine or a-amino-caproic acid and tyocine or

phenyl-p-hydroxy-a-amino proprionic acid. As the members of this series, except tyrosin, are easily soluble in boiling glacial acetic acid, this reagent was added to the concentrated filtrate. A large flocculent, white precipitate was thrown down. This compound was confirmed by Mörners reagent, namely a mixture of 1 part formaldehyde, 45 parts water and 55 parts concentrated sulphuric acid. Upon boiling, this reagent turns green with tyosin. Glycocoll and leucine were tested for by the preparation of their copper salts. Both form slightly soluble blue compounds with copper. Negative results were obtained.

On account of the comparatively large amount of sulphur in keratin, which varies from four to twelve per cent, depending on the source, it would be expected that a large amount of organic sulphur derivatives would be obtained. This was found to

be the case as shown by the formation of a precip-
itate when a soluble lead salt was added to the
distillate.   This precipitate was filtered off and
dissolved in hydrochloric acid after washing.
Hydrogen sulphide was tested for but negative results
were obtained.

The uncondensable vapors after bubbling through
sulphuric acid were also tested, as given above,
passing into a solution of a lead salt with the same
result.   The only derivatives possible in the vapor
would be methyl and ethyl mercaptan boiling respect-
ively at 20^0 and 41^0 and ethyl sulphide boiling at
37.5^0 C.   By fanning the vapor through the lead
salt solution they were deprived of the offensive
odor mentioned.

One of the most interesting facts about the
distillate, especially from a technical standpoint,
is the variation of the total nitrogen content of
distillate, with the methods of heating.   The

analysis of many samples of the distillate from
the gas heated retort showed a total nitrogen con-
tent ranging within the limits of 2 and 3 per cent
calculated on the basis of the total leather used.
Similar analyses made from the distillate obtained
from the electrically heated retort showed a nitro-
gen content of from 4.5 to 6 per cent. It would
seem therefore that the slow steady use in temper-
ature obtained by the electrical heating is pro-
ductive of a better decomposition. According to
the American Leather Chemists Association reports
the percentage of nitrogen in leather varies from
12 to 15 per cent, so that it is quite evident that
some nitrogen must be lost in the elementary form
as will be seen from the following gas analyses.
Distillations with lime, using the gas heated re-
tort, increased the yield of fixed nitrogen about
1 per cent, but completely destroyed the charcoal
which distillation with superheated steam did not
meaterially increase the yield.

Several analyses were made of the gases evolved in order to find if any free nitrogen was evolved. These analyses were made by the ordinary methods of gas analyses, according to Hempel. The analyses were made at the beginning, in the middle and at the end of the runs. Each run extended over a period of five hours. The results are as follows:

No. I was made at the beginning;

No. II was made at the middle;

No. III was made at the end.

Gases	No. I %	No. II %	No. III %
N	27.85	34.22	58.44
CO	8.64	10.95	19.36
CO_2	61.49	31.37	6.21
O	1.63		
Hydrocarbons	0.40	22.95	3.14

The following analyses were made of another
run of about the same length as the above but
divided into four parts:

Gases	No. I %	No. II %	No. III %	No.IV %
N	31.64	29.98	85.27	88.16
CO	5.36	9.53	11.30	9.83
CO_2	41.54	54.22	2.99	1.64
O	2.13			
Hydrocarbons	19.21	6.20		

Several experiments were made on the burn-
power of the gases and it was found that they
would burn very reluctantly.   When passed into a
bunsen flame, they burned fairly readily.

SUMMARY.

1. The above results show that keratin in the form of leather breaks down by destructive distillation into free carbon, ammonia, mono- and d-amino acids, mercaptans and perhaps organic sulphide. These products further dissociate into free nitrogen, carbon monoxide and dioxide, together with a small percentage of volatile hydrocarbons.

2. Of the general primary dissociation products, tyrosin has been proven to be present in quite a large quantity, while leucine and glycocoll if present at all, are in very small quantities, while the phospho-tungstic acid precipitate of di-amino acids has not yet been separated into its constituents.

3. The secondary products are just what would be predicted. According to Mann[1], the

[1]. Chemistry of Proteids, Page 73.

keratin dissociation products vary considerably with the source from which they are obtained, but in general the products are the same as those considered in the above experimental work. All investigators have found an especially large amount of tyrosin with small amounts of glycocoll and leucine and also large amounts of ammonia and mercaptans, especially methyl mercaptan. They have also found large quantities of phenylalanin, $C_9H_{11}NO_2$, which is the only mono-amino acid to precipitate with phospho-tungstic acid under the conditions of the above precipitation so that there is a strong possibility of its presence.

4. It has been shown that the charcoal obtained from the above method is over three times as effective for absorbing material out of solution as ordinary bone charcoal.

5. It has been shown that the leather

decomposes into nitrogenous compounds, the nitrogen content of which equals over 6 per cent of the weight of the original leather.

6.   It has been shown that the percentage of combined nitrogen increases from over 2 per cent obtained by fast and irregular heating to the neighborhood of 500°, to over 6 per cent when the heating is slow and regular up to 420° C.