Analysis and Properties of Old Animal Glues

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Abstract

The old animal glues of hide origin were top quality. They were also very strong and contained a natural fat which prevented foaming. Apart from this it also served as a plasticizer, which made the glue flexible, less hygroscopic and easy to burnish when used under goldleaves. The old hide glues also had a "natural" alkalinity, which reinforced the defoaming effect of the fat. This fat can also be used to determine the animal origin of the glue. The fatty acids present are in fact typical of species, and you only have to know the relative composition of three such acids (saturated ones) to be able to separate most hide glues (assign them to animal species). The fatty acids are myristic acid (14:0), palmitic acid (16:0) and stearic acid (18:0), and the analysis has been carried out on a gas chromatograph. The relative percentages of these fatty acids have also been provided with a joint graphic appearance by means of a rectangular system of co-ordinates. In this each glue obtains its look or profile (gable profile)

Keywords

Animal glues, Fat, Foaming tests, Alkalinity, Acidity, Fatty acids, Gas chromatography, Melting-point tests, Gable profiles.

A vanishing product

In conservation- and restoration science the animal glues have not so far met with the same attention as, for instance, pigments, drying oils etc. Nevertheless they constituted a substantial part of the material used in several crafts in the old times. It seems almost superfluous to tell about their significance for such professional categories as carpenters, cabinet-makers, leather craftsmen, bookbinders, papermakers and others — branches which to-day make use of entirely different adhesives, mostly of petrochemical origin.
In painting, which is my field of action, animal (hide-) glue was used to join boards for panels and their further preparation (isolation, grounding). On the whole the same procedure applied to the preparation of canvas. It also had its given place as binder in distemper, and certain pigments, as for instance ultramarine and azurite, were considered to look their best if bound with a clear hide glue, quite apart from the technique of the rest of the painting.[1] Panels and canvases, though, ar not the only supports that are prepared with animal glue — cardboard and paper are other examples. The reason for their preparation is practically the same, i.e. to stabilize and isolate them in their capacity as support.
To-day we have to face the fact that animal glue, a product which has served artists and craftsmen for such a long time, is practically extinct. In my opinion the reason for this chiefly depends on the exaggerated interest devoted to the artificial resins since their breakthrough in the 1930's. Facing a price-list from the Swedish glue industry in the 1950's, you still get the impression of standing before a flourishing enterprise with a great variety of animal glues. [2] Four decades later you can hardly find any of these factories still in use, i.e. actually producing the glue they are selling.

A wider range of supply in the old days

Which animal glues have been lost then, and which were their properties? First of all the retailers have chosen to emphasize the bone glue, whereas hide glue, which is superior to bone glue in all respects, slowly has disappeared from the shops during the last fifty years. Bone glue is, in fact, a relatively new product in the history of animal glue, and has only been

manufactured for about 150 years. When people for one reason or other are critisizing animal glue to-day, they are consequently referring to the latter product, which in most cases is not top quality. The great variety of animal glues in the old days may best be described by a quotation from *L'art de faire différentes sortes de colle* by Duhamel du Monceau. Besides mentioning a lot of different hide glues, he also talks about a "colle de Flandre" which is said to be good for several "arts":

> This glue does not differ from "la grosse Colle-forte" concerning the way it is made; but since it is used only by distemper painters, manufacturers of broadcloth & for other purposes which do not require a very strong glue & whose principal merit is to be light and transparent, they do not make it like "la grosse colle" called "d'Angleterre", of sinews, ears and hide clippings from old animals, even those from hare, rabbit and from beaver (sic), which will make it red, but of clippings from sheep skins, from lamb skins, or other *young animals* (my italics).

Further on he continues:

> This glue (the Flemish) is far from being as good as "la grosse colle" called "d'Angleterre" for the carpenters, the cabinet-makers, the wood inlayers, but it is preferable for several arts and especially for painters. A glue which is to strong run the risk of falling off like scales; besides "la colle de Flandre" changes the vivacity of the colours less." [3]

Another informant from the same century, Diderot, talks about an eel glue, which he claims to be particularly good for guilding.[4] It is in fact rather fat, and makes the polishing of the applied gold leaves easier.
To be able to fully understand the properties of these old glues I had to make quite a number of them by hand, and according to old manuals. Thus I got valuable experience from glues made out of eel skins, elkhides, cowhides, roe deer hides, sheepskins, goatskins, bream scales, cod bladders and so forth. Unfortunately there is no room in this paper for describing the actual making of the glues and the preparation of the raw material.

Properties connected with fat and pH-value

Despite a great amount of fat being saponified in the manual preparation of the raw material, there will often be enough left to influence the properties of the finished glue in several respects. Modern glue manufacturers remove all traces of natural fat in exchange for de-foaming agents and softening agents, and it is remarkable to notice how they often use the very same substance (fat) as an additive to prevent foaming. The amount of neutral fat in modern glues seldom exceeds 2%. A hide glue with a natural fat content of almost 5 % is most likely to have the following properties: 1) Optimum defoaming effect, which reduces the risk of weakness caused by air bubbles. 2) Acts as an elastic lubricant under goldleaves and facilitate the work of the polishing tool. 3) Makes the dried glue film less hygroscopic and gives it a durable elasticity, since animal fats seldom dries out completely.
To the properies of the old animal hide glues one can also count the fact that they were slightly alkaline, whereas modern ones (mostly of bone origin) seem to have an inclination to acidity The alkaline nature of the old glues increases to a certain limit with every decoction (fraction) of the raw material (glue goods). Basic glue solutions also have a defoaming effect in themselves In the table below the pH-value of two fractions is shown to the left (1 and 3). They have been taken from three animal glues that I have made according to old technology. As a basis for comparison some industrial (animal) glues have been added (D, E, F, G). The measurements have been performed in a 1% glue solution made with destilled water. Solution temperature: +25° C
As measuring instrument a Hellige-meter has been used. To the right of the pH-values stands the foaming ability (Fa) and after that two values on the foaming durability, Fd 3 and Fd 5. They were established in the following way: A 10% glue solution was made with distilled water 40 ml of the test solution was poured in a graded "shaker", i.e a glass cylinder which holds 150 ml The cylinder was put in a thermostat (60±1° C) and eventually shaken in an even rhythm, 30 times up and 30 times down during a period of 30 seconds. Then it was returned to the thermostat After one minute the foam volume=foaming ability (Fa) was red, after three minutes

the first value of the foaming durability (Fd 3) and after five minutes the second value of the foaming durability (Fd 5).

Result

	pH	Fa	Fd 3	Fd 5
A 1	7.85	0	0	0
A 3	8.20	0	0	0
B 1	7.65	0	0	0
B 3	8.39	0	0	0
C 1	7.80	0	0	0
C 3	7.98	2	1	1
D	5.89	23	22	20
E	5.16	1	1	1
F	4.70	50	45	42
G	4.68	20	17	14

A 1 "Colle de Flandre". Made of calfskin which has been prepared with lime and ashes. Fraction 1.
A 3 Same glue, fraction 3
B 1 Glue from goatskin according to Cennino Cennini Prepared with lime and ashes. Fraction 1
B 3 Same glue, fraction 3.
C 1 Hide glue from eel. The raw-material has been prepared with lime Fraction 1.
C 3 Same glue, fraction 3.
D Industrial grain glue of bone origin. Bad quality, bad smell.
E French "hare glue" (rabbit), Chardin Pantin. Hide glue
F Pure gelatin, probably made of pigskins.
G Italian transfer(rentoilage-)glue. Surplus from a painting, 100 years old. From the "Konservatorskolen", Copenhagen. Probably of bone origin.

What is worth noticing in the table above is the practically non-existent foaming of the glues made by hand, and according to old formulae. You can also notice that the weak alkalinity of these glues is relatively greater in the third fraction than in the first one. What does not show in the table, though, is that the glue of the first fraction is fatter than the glue in the third one, but this is something you can see with your naked eye when you handle it. It would not be possible to obtain any zero value concerning the foaming without a relatively high natural fat content. [5] Substantial foaming can be established concerning gelatine, as well as a remarkable acidity. Worth noticing is also the acidity and foaming of the bone glues.

Gas-chromatographic analysis to determine the animal origin of glue

Collaborator and responsible for the chemical operations in connection with this method has been Peter Michelsen, Ass. prof. [6]
Since hide glue from different animals and/or tissues (bone-hide) in most cases show different properties, an important task was to develop an accurate and relatively fast analytical method for glue determination. The one used so far for this purpose has been the determination of amino acid profiles. Instead of applying this relatively limited method, we focused on the natural fat present in, especially, old animal glues Since it has been reported that fatty acid compositions from different animals and tissues differ [7], we found that GC analysis of the fatty acid profiles from the glue fat could be used as an analytical method for glue determination. On the basis of fatty acid methyl esters, fatty acid profiles from about 100 glue samples have been analysed with high-resolution capillary gas chromatography (SP 1000, 23 m, column temp 180°, detector/injector temp 250°, splitratio 1:50), on a Varian Aerograph 3700 gas chromatograph

equipped with a flame ionization detector. Chromatograms were recorded and calculated on a Varian integrator 4370 with a printer plotter.
Concerning the sample preparation, a great deal of care must be taken when lipids are analytically dealt with. Solvents must be free from peroxides and traces of impurities such as undesirable lipids and plasticizers. Therefore they must be distilled before use in such a way that all contaminants are easily and completely disposed of The cleaning cannot possibly be done by passing the solvent through a column of alumina. To prevent unexpected auto-oxidation of sample or solvent, an anti-oxidant such as BHT (butulated hydroxy toluene), 50 mg in 1 litre solvent, can be used. Alternatively HPLC-grade solvent might be used, but it requires a blind test of the solvent, i.e. a test without glue. The removal of solvent is carried out in a stream of nitrogen.
Regarding the preparation of methyl esters there are many methods available for small samples We have tried them all, but we now use borontrifluorid in methanol exclusively, since it is quick and easy to handle

Preparation

1. After having subjected the sample (1-2mg) to conservation treatment (mechanical trimming under microscope), the glue is extracted with distilled water or slightly acidified water (N.B the swelling of the glue) The surplus water is removed , and the fatty acids are liberated with 400 µl 1M KOH in methanol at 60° C for 1 hour
2. At the end of this period, the solution is acidified with 200 µl 5M HCl and heated at 60° for 15 minutes.
3. After cooling, the fatty acids are extracted 3 times with small portions of diethyleter and centrifugalized after each addition
4. The combined ether solution is dried over sodium sulphate and, after filtration, the solvent is removed in a stream of nitrogen.
5. 200 µl 14% BF_3-MeOH is added and heated at 60° for 0,5 hours. After cooling , 2 volumes of hexane followed by 1 volume of water are added. After shaking carefully and centrifugation, the hexane phase is separated and removed in a stream of nitrogen. The sample is then purified on a column of silica eluated with hexane:diethyleter 1:1 (v/v). The solvent is removed again , and the residue is resolved in chloroform and injected into the gas-chromatograph.

Result

The investigation shows that it is not only possible to establish from which animal a certain hide glue originates, but also how to separate it from egg yolk and casein. This can even be done with aged glue, where the unsaturated fatty acids ar more or less broken down. What makes this possible is that you, in most cases, only have to calculate with the relative composition of three saturated fatty acids, namely 14:0, 16:0 and 18:0 (myristic acid, palmitic acid and stearic acid) Initially you only have to use two of them, 16:0 and 18:0, for a preliminary sorting. If it is difficult to determin the animal origin of the glue with regard to these two, the range of fatty acids, primarily 14:0, may be increased to give a more distinctive result. In the table below I present what I mean by "safe glues", i.e glues that I have either made myself according to old formulae or those which have been controlled in such a way that their identity cannot be questioned (meltingpoint tests). Heinrichs' method has been used to perform these tests [8] This means that you use 80 mm long, thin walled meltingpoint tubes, 4-5mm in diameter. Such a tube is filled with glue solution, in this case of 12,5%, to a level of 5 mm. The solution is allowed to gelatinize at a temperature of 10° C during a fixed time (one hour). After that the tube is attached to a thermometer, which is plunged 30 mm in a beaker with cold vater The water is then gradually heated After a while when the jelly plug begins to melt, it ascends towards the surface, and at that moment the temperature is red. Generally you can say that bone glue is to be found in the lower part of the register (22-25° C), and hide glu in the upper (26-35° C) Below the table there is an arrangement of the origin of the glues.

Fatty acids, rel. %	16:0	18:0	14:0	16:0	18:0	melt. p.
1. hide glue, cattle	59,3	40,7	8,5	54,3	37,2	-
2. hide glue, cattle	62,1	37,9	8,3	57,0	34,7	-
3. hide glue-calf	64,5	35,5	8,7	58,9	32,4	31°
4. bone glue, cattle	56,6	43,4	4,6	54,1	41,3	-
5. bone glue, cattle	62,3	37,7	4,2	59,7	36,1	22°
6. bone glue, cattle	59,1	40,9	3,7	57,0	39,3	23°
7. hide glue, sheep	54,2	45,8	4,4	57,8	43,8	-
8. hide glue, sheep	57,0	43,0	6,0	53,6	40,4	-
9. hide glue, rabbit	77,0	23,0	5,9	72,5	21,6	-
10. hide glue hare	78,3	21,7	11,4	69,3	19,2	30,5°
11. hide glue, hare	78,2	21,8	8,6	71,5	19,9	30°
12. hide glue, goat	69,9	30,1	12,2	61,4	26,4	34°
13. hideglue, elk	57,8	42.2	23.3	44,3	32,4	35°
14. hide glue, eel	80,0	20,0	19,5	64,4	16,1	-
15. casein	83,9	16,1	31,1	52,9	16,0	-
16. egg yolk	77,7	22,3	1,7	76,4	21,9	-

1. Handmade hide glue from cattle. The raw materia (glue goods) has only been carefully washed. No other preparation, neither alkaline nor acid, has been performed. Surplus fat clearly visible on the first fraction (crust). Own manufacture.
2. Handmade hide glue from cattle. The glue goods has been prepared with lime for a week , after which it has been carefully washed. Surplus fat clearly visible on the first fraction (crust). Own manufacture.
3. "Colle de Flandre". Handmade glue from calfskin. Prepared with lime and ashes. Own manufacture.

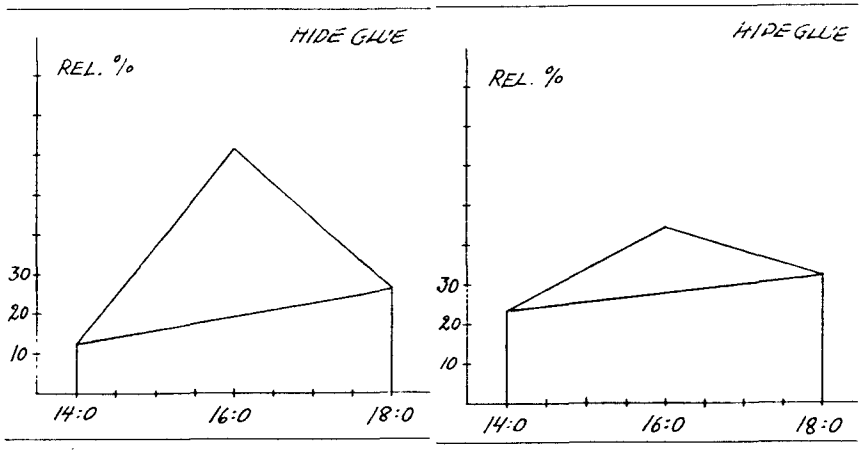
4. Handmade bone glue from cattle, which has been prepared with lime (1 part) and ashes (3 parts). In this solution the glue goods (crushed bone material) has been soaking for a week, after which it has been carefully washed and boiled down. Own manufacture.
5. Industrial bone glue (cake) made by Sandvik (Swedish Bone-Meal Ltd.).Stamped "Extra". From the Museum of Cultural History, Lund. The bone glue identity has been determined by meltingpoint test.
6 Industrial bone glue stamped "Kronlim"— probably also from Sandvik. From the Museum of Cultural History, Lund. The bone glue identity determined by meltingpoint test.

7. Handmade hide glue from sheep. Prepared, wet glue goods (liming) from the Kid Leather Factory Ldt., Kävlinge. Carefully washed before boiling. The first fraction of the glue rather fat. Own manufacture.
8. Handmade hide glue from sheep. The glue goods received from the Kid Leather Factory Ldt., Kävlinge as dry and salted clippings. The first fraction of the glue rather fat. Own manufacture.

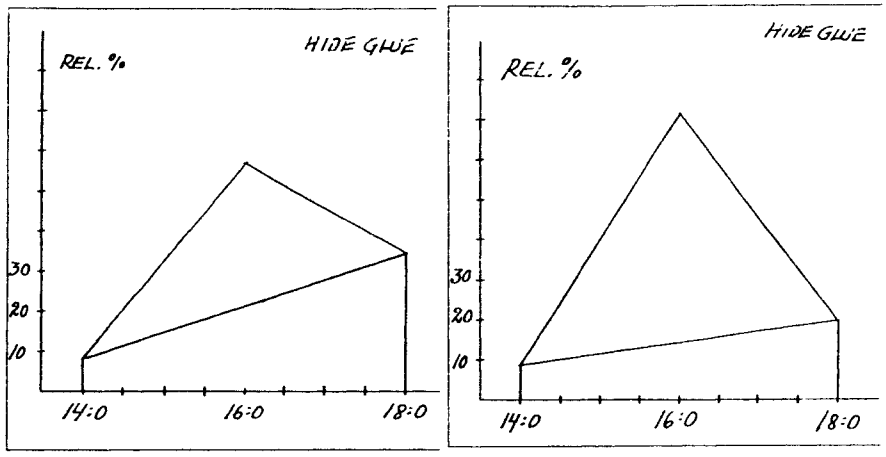
9. Handmade hide glue from rabbit. The skin was put in pure water for a week, after which it was transferred to a lime and water mixture until the hairs loosened. After that it was washed and boiled down.
10. Industrial "hare glue" in the form of a cake, stamped Chardin Pantin. Probably made from rabbit skin. Approximately 50 years old.

11. Industrial "hare glue" (hide origin) Probably the same manufacturer as under 10, but no sign of a stamp can be found on the piece of glue from which the sample comes
12 Handmade glue from goatskin. Prepared with 1 part of lime and 3 parts of ashes in water for about a week, or until the hairs loosen. The first fraction of the glue rather fat.
13. Handmade hide glue from elk. Prepared, wet glue goods from the Kid Leather Factory Ltd in Kävlinge (soaking in lime and water for a week). Own manufacture.
14. Handmade glue from eelskin. Acid preparation with Druvan's colourless and biological vinegar (12%). The glue seems fat. Own manufacture.
15. Industrial casein in powder.
16. Egg yolk.

It becomes quite clear, if you look only at the fatty acids 16:0 and 18:0 in the table above, that certain glues are impossible to separate. Hide glue and bone glue from cattle have similar values, and these, on their part, correspond quite well to the values of hide glue from sheep and hide glue from elk. Hide glue from hare (rabbit) and egg yolk also show corresponding values. On the other hand each one of the glues mentioned differs from hide glue-goat, hide glue-eel and casein If you exclude bone glue, which is a young member of the family, and add 14:0 (myristic acid) to the relative composition of the fatty acids, you will find a small difference between hide glue from cattle and sheep, whereas it becomes quite obvious between cattle and sheep on one side and elk, hare, goat, eel and casein on the other. Thus the glues in the table are separated, of course with a a certain reservation for the glues from cattle and sheep, which come quite close in values
It may seem a little abstract to draw parallels between the different glues only on the basis of the percentages above. Therefore these relative percentages of the fatty acids have been provided with a joint graphic appearance by means of a rectangular system of co-ordinates. In this each glue obtains its look or profile (gable profile — see pictures 1 and 2).[9]



1 The fatty acid composition of goat glue illustrated by gable profile (left picture). To the right gable profile which illustrates the fatty acid composition of elk glue.



2. To the left the fatty acid composition of glue from cattle illustrated by gable profile, and to the right; gable profile illustrating the fatty acid composition of hare glue (rabbit)

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1 Cennino Cennini, *The Craftsman's Handbook "Il Libro dell'Arte"*, transl. by Daniel V. Thompson, New York 1960 (1933), p 68.

2 "Prislista å draglim" from the Gluemanufacturers Limited, April 20 th 1953.

3 Duhamel du Monceau, *L'art de faire différentes sortes de colle*, Paris 1771, p 14.

4 *Encyclopédie ou Dictionnaire Raisonné des Sciences, des Arts et des Métiers* (ed. by Diderot et d'Alembert), Tome troisième, Paris M.DCC.LIII., p 626

5 Saur has pointed out the connection between alkalinity and low foaming values. The foaming is at its peak at a pH-value of 7,5 (32,2 ml) and decreases then both in the acid and the basic direction – most in the basic one, though. A pH-value of, for instance, 8,9 gives a foaming durability (after 3 minutes) of 10,2 ml, whereas pH=3,5 gives one of 24,3 ml. This is a clear indication that the alcalinity has a de-foaming property of its own. To be able to reach a foaming durability of zero it has to be helped by the natural fat in the glue. E. Sauer, *Chemie und Fabrikation der tierischen Leime und der Gelatine*, Berlin, Göttingen, Heidelberg 1958, p 86.

6 For correspondence Dr. Michelsens adress is: Egnahemsvägen 8 c, S-232 39 Arlöv, Sweden

7 A. Kuksis, *Handbook of Lipid Research*, New York, London 1978, p 84 ff. See also P.N Williams, *The Chemical Constitution of Natural Fats*, London 1964, p 1 ff.

8 Sauer, Op cit, p 299 f.

9 Bengt Skans, *Vad säger oss altarskåpen i Ö. Vram* (English summary) Lund 1991, p 158 ff.

Zusammenfassung

Die alten Hautleime waren von sehr guter Qualität Sie waren auch sehr stark und enthielten einen natürlichen Fett der die Schäumung verhinderte. Ausserdem diente der Fett als einen Weichmacher, der den Leim flexibel, weniger hygroskopisch und leicht unter Goldblättern zu polieren machte. Die alten Hautleime hatten auch einen "natürlichen" Alkalität, der den Schaumdämpfenden Effekt des Fetts versterkte. Dieser Fett kann auch zur Bestimmung der animalen Abstammung des Leims angewendet worden. Ermöglicht wird dies, weil die im Fett enthaltenen Fettsäuren arttypisch sind, und die relative Zusammensetzung von nur drei gesättigten Fettsäuren bestimmt werden muss, um die meisten Hautleime separieren zu können (Ursprungsart festzustellen). Die Fettsäuren sind Myristinsäure (14:0), Palmitinsäure (16:0) und Stearinsäure (18:0), und die Analyse war auf einem Gaschromatograph ausgefürt Mit Hilfe eines rechteckigen Koordinatsystems sind die relativen Prozentsätze dieser Fettsäuren mit einem gemeinsamen Aussehen versorgt. In diesem System bekommt jeder Leim sein Aussehen oder Profil (Giebelprofil).