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LEATHER TECHNOLOGY CENTRE

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CHINA

Technical report: Leather fat-liquoring

Prepared for the Government of China
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of K. J. Bieńkiewicz, expert
in leather chemistry

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Vienna

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ABSTRACT

As part of the ongoing project "Leather Technology Centre" (DP/CPR/83/004), a leather chemistry expert was assigned to the project for three weeks, beginning on 9 June 1986, which was extended to four weeks.

The purpose of his mission was to present current knowledge on the preparation of fat-liquors and the fat-liquoring of leather to staff of the Leather Technology Centre (LTC) and various institutions in China. To achieve this aim, the expert gave a course consisting of a series of lectures, seminars, discussions and laboratory demonstrations.

The expert recommends starting a research programme at the LTC, in co-operation with other institutions, in which the problems of fat testing and evaluation would be included and the number and range of fat-liquors extended.

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INTRODUCTION

Until recently, domestically produced fat-liquors in China have been sufficient to satisfy the demand of tanneries producing leather for domestic use.

Tanneries are now expected, however, to produce more and more leathers for export and require much higher quality fat-liquors, which are not available domestically.

Within this context, and as part of the ongoing project "Leather Technology Centre" (DP/CPR/83/004), a leather chemistry expert was sent by the United Nations Industrial Development Organization (UNIDO), acting as executing agency for the United Nations Development Programme (UNDP), to China for a mission of three weeks, beginning on 9 June 1986, which was extended to four weeks.

According to his job description (annex I), the expert was expected to assist and advise his national counterparts at the Leather Technology Centre (LTC) on ways to improve the quality of fat-liquors and to develop new products, as required by the tanneries. The expert was also expected to elucidate theoretically the mechanism of the reaction between fat-liquor and collagen fibres during pickling, tanning, fat-liquoring, drying etc. and to determine the influence of these processes on the physical and aesthetic properties of the resulting leather.

The expert gave a comprehensive course, which consisted of a series of lectures covering the topics given in his job description. The lectures were well attended and, together with seminars and discussions, occupied much of the expert's time.

Owing to a shortage of time, laboratory experiments were concentrated on refining secondary lard, and refining and deodorizing fish oil. In general, the experiments were successful, although more experiments, time, facilities and chemicals are required to obtain satisfactory results.

The expert recommends starting a research programme at the LTC, in co-operation with other institutions, in which the problems of fat testing and evaluation would be included and the number and range of domestic fat-liquors extended.

RECOMMENDATIONS

To the Leather Technology Centre

1. There are four possible sources of raw materials for the production of fat-liquors: (a) synthetic components; (b) secondary lard; (c) mixed fish oil; and (d) rape-seed oil. The quality of sources (b) and (c) still needs further improvement, and a systematic investigation, both technological and analytical, should be implemented. A technological investigation should help to determine the best way to improve the quality, as demonstrated during the mission. Source (d) should be modified by chlorination. The analytical investigation should consist of several tests, as described below, carried out systematically on every batch in order to recognize the relationship between the technological applicability and the analytical characteristics of raw materials used in the pilot plant.

2. The LTC should initiate close co-operation with the Institute of Organic Chemistry of the University of Shanghai or with another institute at the university level in order to identify and investigate the components of top quality fat-liquors. This requires specialized, expensive facilities (infra-red, nuclear magnetic resonance and mass spectrometers, chromatograph etc.). These instruments would not be used continuously, so it is not recommended that they be purchased for the LTC. Besides, they require specialized staff to operate them and to interpret the results. The experience of such staff would not be useful in the everyday work of the LTC.

3. To obtain fat-liquors that are not produced at present, it is suggested that the possibility of producing non-ionic fat-liquors be investigated with representatives of an oil refinery. For example, ethoxylated derivatives of fatty acids and alcohols are currently very important in the production of garment grain and suede leather. Ethoxylated derivatives of alkylphenols, and others, are components of such fat-liquors.

4. The research programme of the LTC should include an extensive investigation of domestic lanolin, including its chemical modification, which is not used at present in the Chinese leather industry. Similar results may be obtained by investigating higher boiling point (over 240 °C) fractions of crude oil containing some waxes and fatty alcohols.

5. The possibility of investigating derivatives of phosphoric acid should be considered. A typical example of such a derivative is lecithine, a component of egg yolk. Phosphorus-containing components are now used in the production of synthetic fat-liquors, replacing the egg yolk used in older technologies.

6. The input of the LTC to industry should be increased. This could be achieved by creating incentives for factories to implement technological methods worked out at the LTC. From this point of view, recommendations made in an earlier report (DP/ID/SER.A/654) concerning proposed changes in industrial processes and co-operation between the LTC and factories should be reviewed.

7. It is strongly recommended that the results of research work done at the LTC should be published in recognized journals. It is also advisable that the LTC start its own journal or newsletter, where its activities could be presented, together with review papers translated or abstracted from foreign journals, some advertisements etc. This journal could be bilingual, in Chinese and English, in order to be accessible to a wider readership. It would also give Chinese readers the possibility to become familiar with world progress in the leather and leather products industry.

To UNIDO

8. Implementing the above recommendations in the research programme of the LTC would require periodic supervision by a specified scientist acquainted with programme preparation and implementation.

I. ACTIVITIES

The exact programme of activities to be carried out during the mission was agreed upon with Mr. Shi Xianglin, the National Project Director of the Shanghai Leather Research Institute (SLRI), after arrival in Shanghai and consisted of:

(a) Lectures;

(b) Seminars (discussions) relating to the problems covered in the lectures;

(c) Laboratory experiments;

(d) Visits to two factories, the Chemical Works in Shanghai and the Hong Kwang pigskin tannery.

The expert had also intended to visit the Institute of Organic Chemistry of the University of Shanghai, but it was not possible to arrange the visit within the time available.

A. Lectures

The lectures covered the topics given in the expert's job description (annex I). Thirty people from various factories and institutions in China attended the lectures and took part in seminars, experiments and discussions. The detailed programme of the lectures was as follows:

(a) The fate of fats throughout the tanning process. How and to what extent natural fats are changed during storage of raw stock and removed from hide or skin in beamhouse operations. When and why fats have to be included in the tanning process and how they react with leather components (particularly collagen), tanning agents, auxiliaries, finishes etc.;

(b) The chemistry of fats and their technological and physical properties. Changes in fats during the preparation of fat-liquors, the theory of emulsions, lubricating functions in leather and the consequences of aging during storage and wear. The composition and characteristics of natural fats from various origins;

(c) Distribution of fats in leather as a result of the chemical activity of particular components. Fat migration and its consequences in the shoemaking process and the occurrence, removal and prevention of fatty spews on leather surfaces;

(d) Characterization of fats by commonly used methods, such as pH, saponification and iodine values, and by more advanced and informative methods, such as the Panzer-Niebühr method, infra-red spectroscopy, liquid-liquid chromatography and the use of specific reactions for identifying particular components or the presence of charateristic functional groups. Interpretation and explanation of the results of analyses of samples from the Chinese fat industry, submitted by the LTC to the consultant and tested before the mission;

(e) Methods of preparation of natural fats for use as fat-liquor components: refining, deodorizing and bleaching, as carried out on an industrial scale. Basic methods for evaluating process effectiveness: freezing point, colour testing, pH and stability of standard emulsions;

(f) Chemical methods for transforming fat: oxidation, sulphonation, sulphatation, sulphitation, chlorination, sulphochlorination, phosphorization, transesterification, polymerization, and the reduction of fatty acids to alcohols as unit operations in the fat industry. Further processing of such transformed fats to more complex compounds containing more functional groups of specific character, e.g. amines, phenols and dicarboxylic acids; Mannich's reaction;

(g) Preparation of fat-liquors from basic components for different destinations. Auxiliary components, such as buffers, solvents, preservants and stabilizers. Significance of storage and transportation temperatures. Influence of other factors on tanning and finishing operations;

(h) Methods of evaluating fat-liquors: sulphur trioxide content (bound and total), emulsion stability against water, hard water, tanning agent solution and salt solutions, methods of determining the ratio emulsifier/emulsifiant. Components of the emulsifier and the emulsified substance. Trends in contemporary production of fat-liquors: standardization of the components, replacement of rare natural fats like sperm whale oil or copra oil by synthetic products, use of succinylates, production of combined-function derivatives like compounds of chromium with fatty acids, use of secondary raw materials (reuse of offal), fat-liquors for special products such as softy and nappa leathers, non-yellowing fat-liquors for white leather.

It should be noted that the composition of some commercially produced fat-liquors could not be obtained since they are trade secrets, are frequently patented through a very wide range of components, or are masked by the addition of some components that have no technological significance but that make accurate identification almost impossible.

B. Seminars and discussions

The seminars and discussions occupied much of the consultant's time, as participants of the course showed particular interest in certain topics. Some of the participants were very qualified, particularly those from the LTC and from the Chemical Works. The consultant is convinced that translations of the lectures and seminars (done by Mr. Peng Shang Zhi from the Shanghai Leather Products Corporation, Foreign Economic and Technical Co-operation Department) were very accurate and highly professional. This may be concluded from questions asked, which covered both the technological side of manufacturing and the theory of the processes, and also from answers given to the consultant's questions.

C. Laboratory experiments

As there was little time available for laboratory work, experiments were concentrated on three topics:

(a) Refining secondary lard;

(b) Refining fish oil;

(c) Deodorizing fish oil.

Secondary lard. collected from pigskins, is rather dark and has a very characteristic smell. It was demonstrated to the participants, that an odourless lard can be obtained by sponifying the free fatty acids in the

secondary lard. This is achieved by adding 3-4 per cent of a 15 per cent solution of sodium hydroxide, separating, acidifying to about pH 2 and subsequently washing out the fatty acid products. It was shown that a quite colourless lard could be obtained by heating with a small amount of charcoal (this had to be used, as other bleaching agents, like activated clay or bentonite, were not available). The resulting lard may be used in fat-liquors for white leather.

Crude fish oil was refined with great difficulty, as it contains a large amount of protein. Using a method similar to that for refining lard gave either poor yield or unsatisfactory results. To separate the refined oil properly and with satisfactory yield from soapstock formed during the refinement process would be possible with the use of a laboratory centrifuge of the washing machine type, but this was not available at the LTC. Much more time, facilities and chemicals would be required to obtain satisfactory results. No bleaching experiment was undertaken with fish oil.

Some positive results were obtained in experiments to deodorize crude fish oil. It should be pointed out, however, that it was only possible to demonstrate the principle of the method using an improvised apparatus, in which water vapour was blown through the oil in order to denature and precipitate proteins and to remove foul-smelling lower fatty acids, which are volatile during steam distillation. There was no possibility to use the usual procedure with superheated steam (at 180 °C, followed by evacuation to a pressure of 6-8 mmHg). Some improvement was observed, however, in the properties of treated oil. It separated better than the crude oil from the soapstock produced in the subsequent alkaline process and its smell was distinctly less offensive, though still present. It was proposed that the staff of the chemical laboratory of the LTC continue this experiment on a laboratory-scale apparatus (a scheme for such an apparatus was provided by the consultant, together with instructions on its use).

D. Factory visits

Approximately 20 participants visited the Chemical Works in Shanghai and the Hong Kwang pigskin tannery. An evaluation of the factories was made later, although some advice was given during the visit to the Chemical Works. An evaluation of the pigskin tannery is given below.

II. FINDINGS

A. Domestic production of fat-liquors and the availability of raw materials

According to the participants of the course given during the mission, who represent factories (in Shanghai, Lu Zhan, Dan Dong, Beijing, Tian Ting, Wu Han and Tian Zhu) producing chemicals for the leather industry, the country's annual fat-liquor requirements are around 10,000 tons. At present, 6,000 tons are produced and 250 tons are imported. The figures appear doubtful when compared with the number of animals slaughtered (given in project documents and in several job descriptions attached to the project file):

	Number (millions)	Approximate weight (tons)
Cattle hides (including buffalo)	5	100 000
Goats and sheep	30	150 000
Pigskins	50	250 000
		500 000

It should be taken into account, that a certain quantity of goat and sheepskins may be exported as raw skins, and that probably not all pigskins are recovered after slaughter. It was not possible to have the figures confirmed by the Ministry of Light Industry. Accepting the above value, however, and taking 50-60 per cent of this amount as shaved weight (splits included) gives a total rawhide/skins weight of 250,000-300,000 tons. Thus 10,000 tons of fat-liquor do not appear to be adequate, since the use of 3-4 per cent fat-liquor on shaved weight would not suffice. Usually, at least 5 per cent fat (6-7 per cent fat-liquor) is necessary, and even more for small skins. It was not possible during the seminars to find out how this serious deficit, which according to the above calculation is more than 60 per cent, is covered or replaced in the leather industry.

At present, fat-liquors are produced only from synthetic materials. Small amounts of secondary lard from fleshing of the pigskins are, however, used as fat-liquor components in pilot-plant-scale production in the LTC. According to information obtained during discussions with course participants, only three natural fats are of interest: secondary lard, mixed fish oil and rape-seed oil. Other resources are generally unavailable, since genuine lard, tallow and poultry fat are used for consumption and vegetable oils are consumed or exported.

Collecting lard from pigskins is possible on an industrial scale, although if this process were to be introduced, it should consist of lard collection together with reuse of proteins from the gluestock and trimmings, which may serve as good poultry and pig feeding material. Such methods are well-known and widely used and can be applied in larger tannery units. Collecting lard simply by melting offal in an open pot is less economic and gives unrefined material.

It was demonstrated with test samples that fish oil is of very poor quality, requires deodorization and refining, and perhaps bleaching, although the last operation is questionable. Deodorized and refined fish oil might be used as a component of fat-liquor for dark leather.

The use of rape-seed oil for preparing fat-liquors requires some caution, because it contains 30-40 per cent erucic acid, which oxidizes and polymerizes easily on leather, causing hardness and roughness during storage.

In the consultant's opinion, the natural fats discussed may have better properties after oxidation and chlorination; however, further research by the Chemical Works, in co-operation with the LTC, is required.

The production of domestic fat-liquors may be increased by:

(a) Collecting and refining secondary lard;

(b) Improving the production of fish oil;

(c) Increasing the production of synthetic components.

B. Quality of domestic fat-liquors

The results of tests done on domestic fat-liquors before the mission (annex II) were given to the course participants. Generally they do not differ much from other products of this kind, having appropriate emulsion stabilities and indices (iodine, acid and saponification values). Transparent oil and fat-liquor SYN may be used for white leathers, with the addition of good quality lanolin from domestic sources (0.5-1.0 per cent on shaved weight) to give a silky feel to the leather. Products from the pilot plant of the LTC were not presented for evaluation.

C. Factory evaluations

Only one chemical factory was visited during the mission. It is in good order, supplying products of acceptable quality but limited in range: six anionic and only one cationic product with no non-ionic and no amphoteric products. To increase the range of fat-liquors produced would require research work to be undertaken between the LTC and an oil refinery, or the purchasing of know-how from foreign producers. In the consultant's opinion, such a purchase would only be possible from smaller producers, since larger and more well-known companies usually only sell their products, not their knowledge and expertise.

The leathers produced by the Hong Kwang pigskin tannery are rather low quality and cannot be considered to be exportable products. A basic revision of the technological processes used would be necessary to achieve an international standard; the use of top quality fat-liquors alone would not produce the desired results. Close co-operation with the LTC could help, however, as the products of the LTC pilot plant are much better.

Annex I

JOB DESCRIPTION

Post title: Expert in leather fat-liquors

Duration: Three weeks

Date required: Mid-1986

Duty station: Shanghai

Purpose of project: To assist and advise national counterparts by transferring modern expertise and knowledge in order to improve the quality of fat-liquors now being produced in the country, and to develop new products as required by the tanneries. The expert will also be expected to elucidate theoretically the mechanism of the reaction between fat-liquors and collagen fibres during pickling, tanning, fat-liquoring, drying etc. and their influence on the physical and aesthetic properties of the resulting leather.

Duties: The expert will be expected to inform national counterparts about the following:

(a) Testing methods for the characterization and determination of different fat-liquors;

(b) The characteristics, chemical constitutionand general methods of preparation (if possible) of fat-liquors for the following types of leather:

(i) Softy leather and garment leather;
(ii) Water repellent leather;
(iii) Suede leather, to impart a silky sheen, water repellency and deep colour;
(iv) Light-fast white leather;
(v) Vegetable leather.

(c) Techniques of refining, deodorizing and sulphitation of mixed fish oil;

(d) Methods of preparation of fat-liquor constituents, such as alkyl sulphonates, carbonic acid amide derivatives, sulpho-succinate derivatives, aliphatic polyglycol phosphoric acid esters, long chain phosphoric acid esters, alkyl oxide adduct derivatives, sulphoester derivatives with long chain glycerides and alkanes;

(e) The chemical reaction of fat-liquors with collagen fibres and their influence on tanning, dyeing, retanning, drying and finishing, and on the physical and aesthetic properties of the resulting leather;

(f) Recent trends in fat-liquor products.

Qualifications:	The expert should have a profound theoretical knowledge of and extensive practical experience in the methods of preparation and application of the various types of fat-liquor used in tanning processes.
Language:	English

Annex II

EVALUATION OF FATS AND FAT-LIQUORS SUBMITTED FOR TESTING

The chemical analyses, carried out according to Polish standards, which are based on standards of the International Organization for Standardization (ISO), of samples submitted for testing are given in annex table 1.

There are no deviations from generally accepted values and the fat-liquors and raw materials produced from them are good quality. Raw fish oil had the highest iodine value, although this decreased to an acceptable level after sulphitation.

The stability of fat-liquor emulsions in standard solutions (annex table 2) is satisfactory and they can be used without difficulty.

An evaluation of the infra-red spectra of the fat-liquors shows that fat-liquor SYN and fat-liquor SE are almost identical, with only a slight difference in the ratio of different groups (NH_2 and SO_3). Fat-liquor SF is of the same type, although the similarity is less marked.

Fat-liquor from fish oil and leather-softening fat-liquor are also similar. The leather-softening fat-liquor contains more NH_2 groups but has a very similar chemical composition to that of fish oil.

Fat-liquor 805 is a mixture of aliphatic long-chain components and contains OH and CO groups of an ester type (perhaps from rape-seed) and a relatively large amount of SO_3 groups.

Cationic fat-liquor contains many NH_2 groups and is not, or only very slightly, sulphonated.

None of the spectra presented (figures I-VII) show the presence of aromatic rings. It was not possible to confirm whether the products had been lightly chlorinated.

All the results obtained concern the samples provided, as neither the method of sampling nor the sampling protocol were given to the consultant.

Table 1. Chemical analyses of fats and fat-liquors submitted for testing

Product	Saponification value (mg KOH/g)	Iodine value (gI_2/100 g)	Acid value (mg KOH/g)
Sulphited fish oil	157.3	53.2	21.9
Fat-liquor SYN	85.5	20.8	36.2
Transparent oil	181.7	37.9	56.0
Fat-liquor SF	37.1	16.8	33.6
Fat-liquor from fish oil	154.7	45.8	57.3
Raw fish oil	172.4	114.4	56.9
Fat-liquor SE	41.7	6.6	29.3
Fat-liquor 805	102.8	43.9	31.6
Rape-seed oil	168.7	89.2	3.9
Petroleum alkane, C=15	0	2.1	0.9
Cationic fat-liquor	91.9	1.0	3.8
Synthetic neatsfoot oil	181.8	61.7	0.4
Leather-softening fat-liquor	91.6	29.4	54.4
No. 5 mineral oil	0.7	11.2	0.1

Table 2. Emulsion stability of tested fat-liquors

Product	Water	Hard water	Tanning agent
Fat-liquor SYN	+ +	+ +	+
Fat-liquor from fish oil	+ +	+ +	+
Fat-liquor SF	+ +	+ +	+
Fat-liquor SE	+ +	+ +	+
Fat-liquor 805	+ +	+ +	+
Cationic fat-liquor	+ +	+ +	+

Figure 1.
Infra-red spectrum of fat-liquor SYN

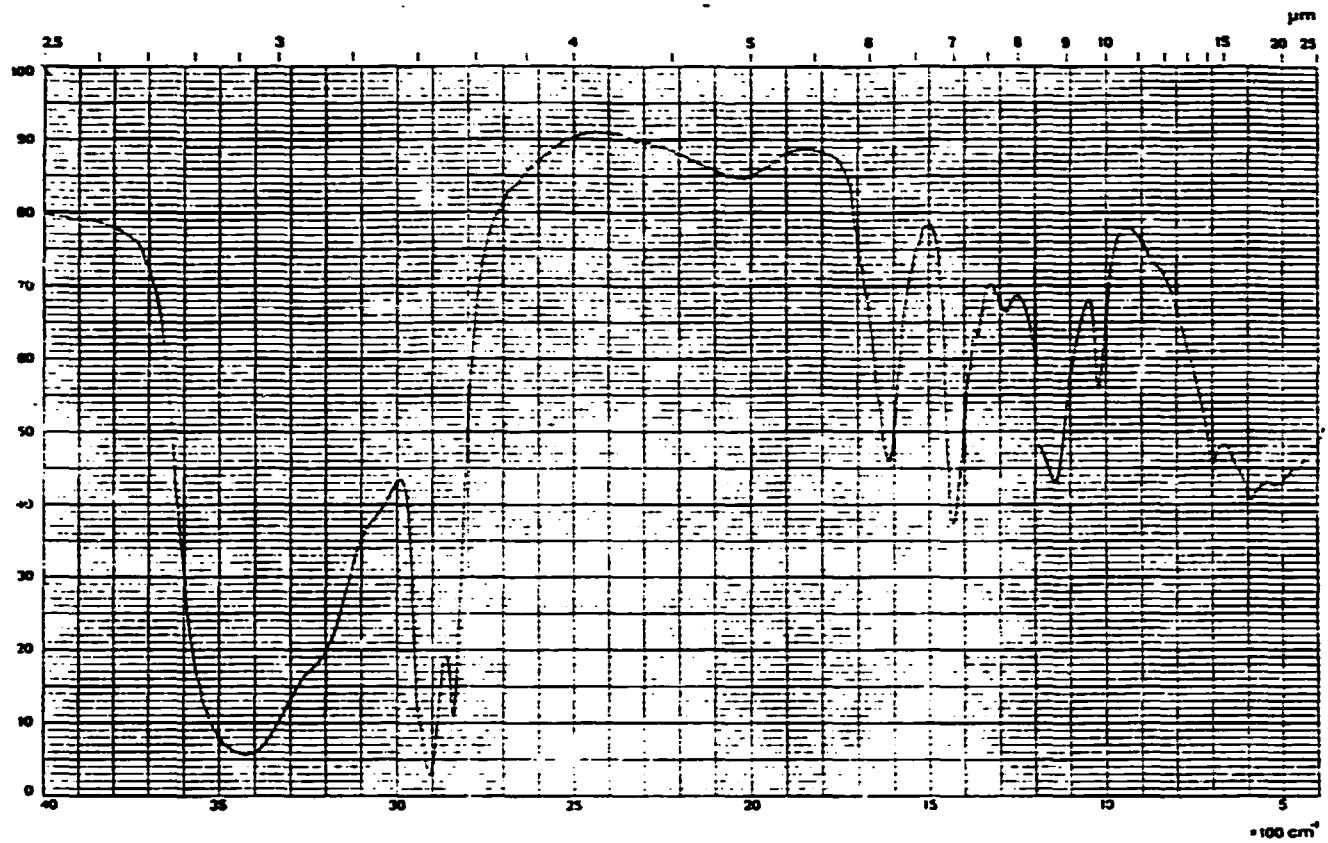

Figure 2.
Infra-red spectrum of fat-liquor SF

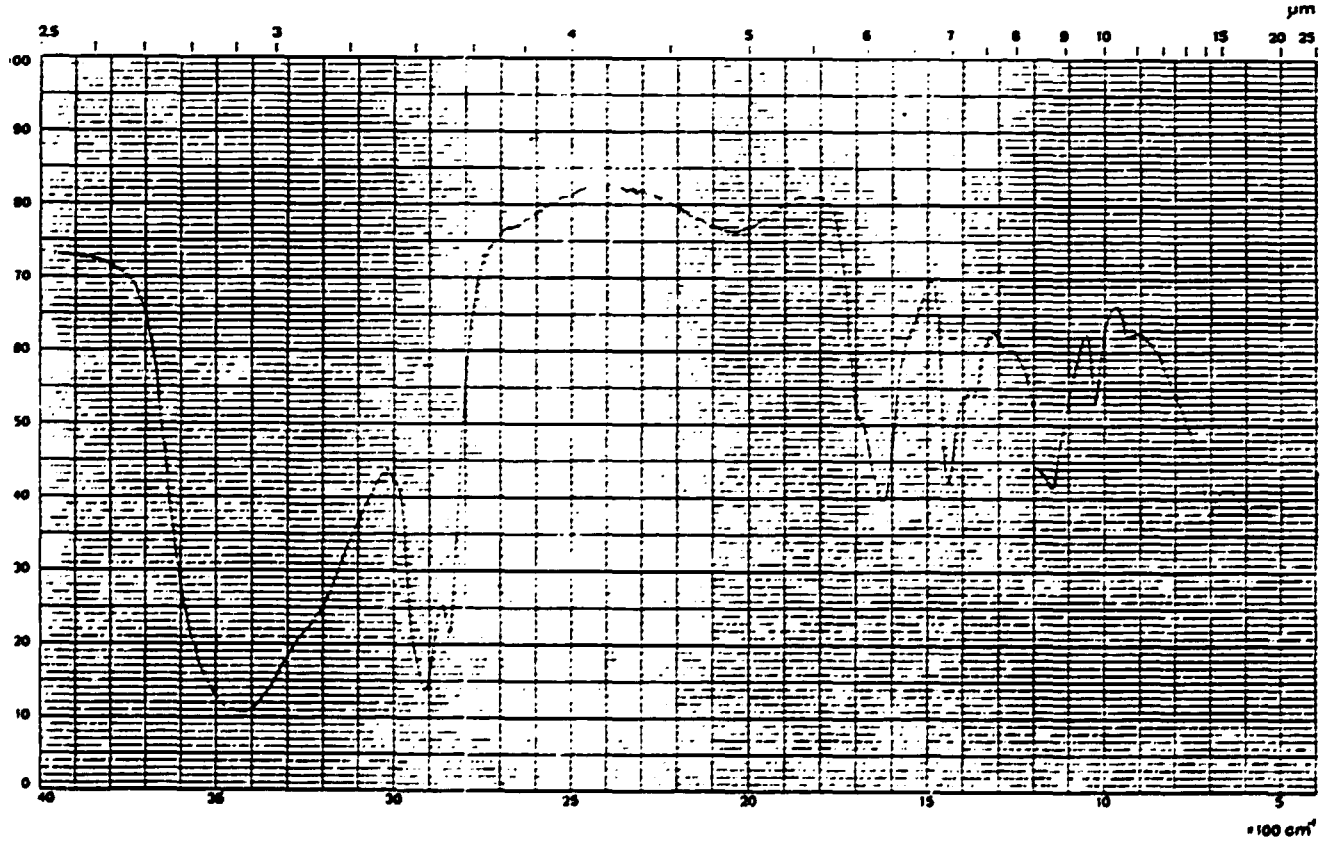

Figure 3.
Infra-red spectrum of fat-liquor SE

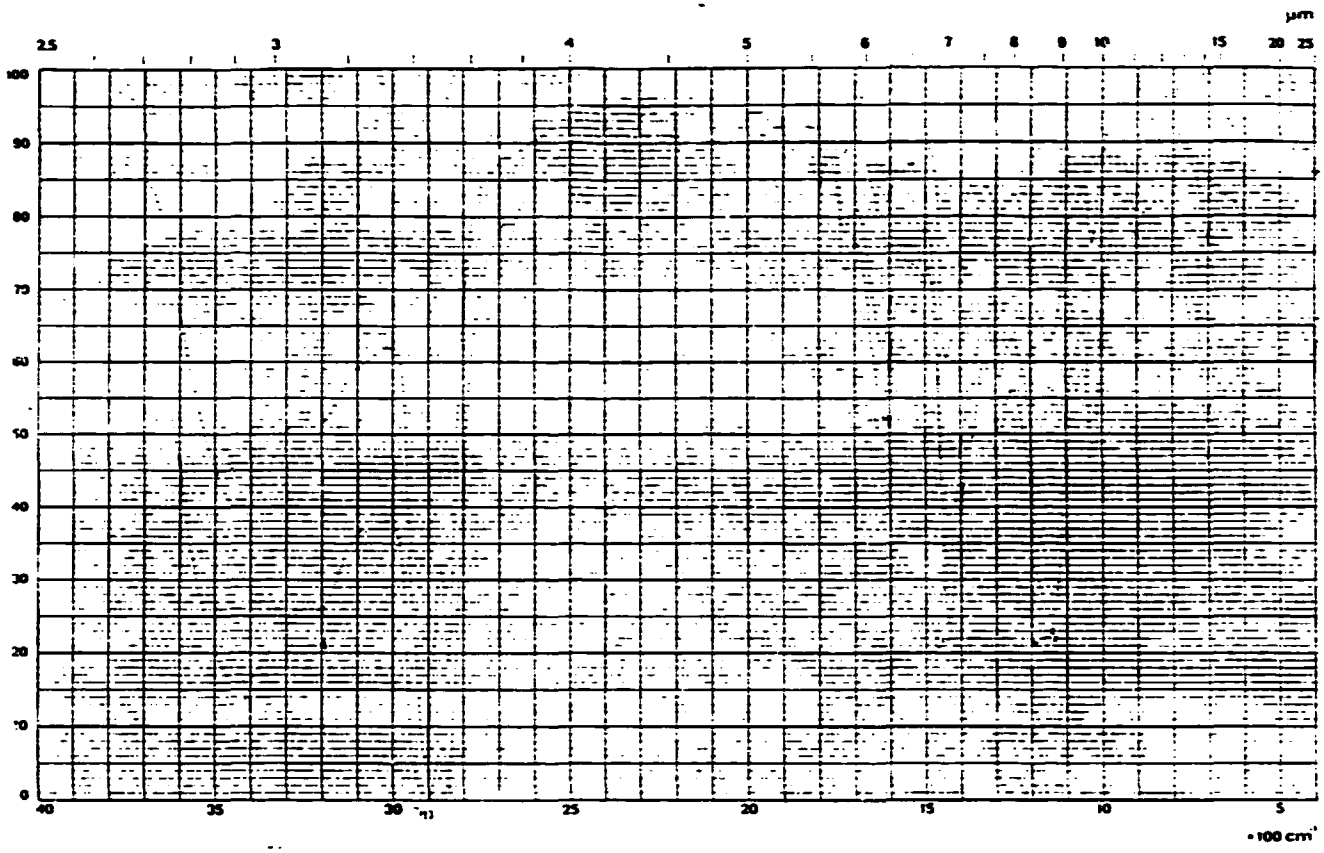

Figure 4.
Infra-red spectrum of fat-liquor from fish oil

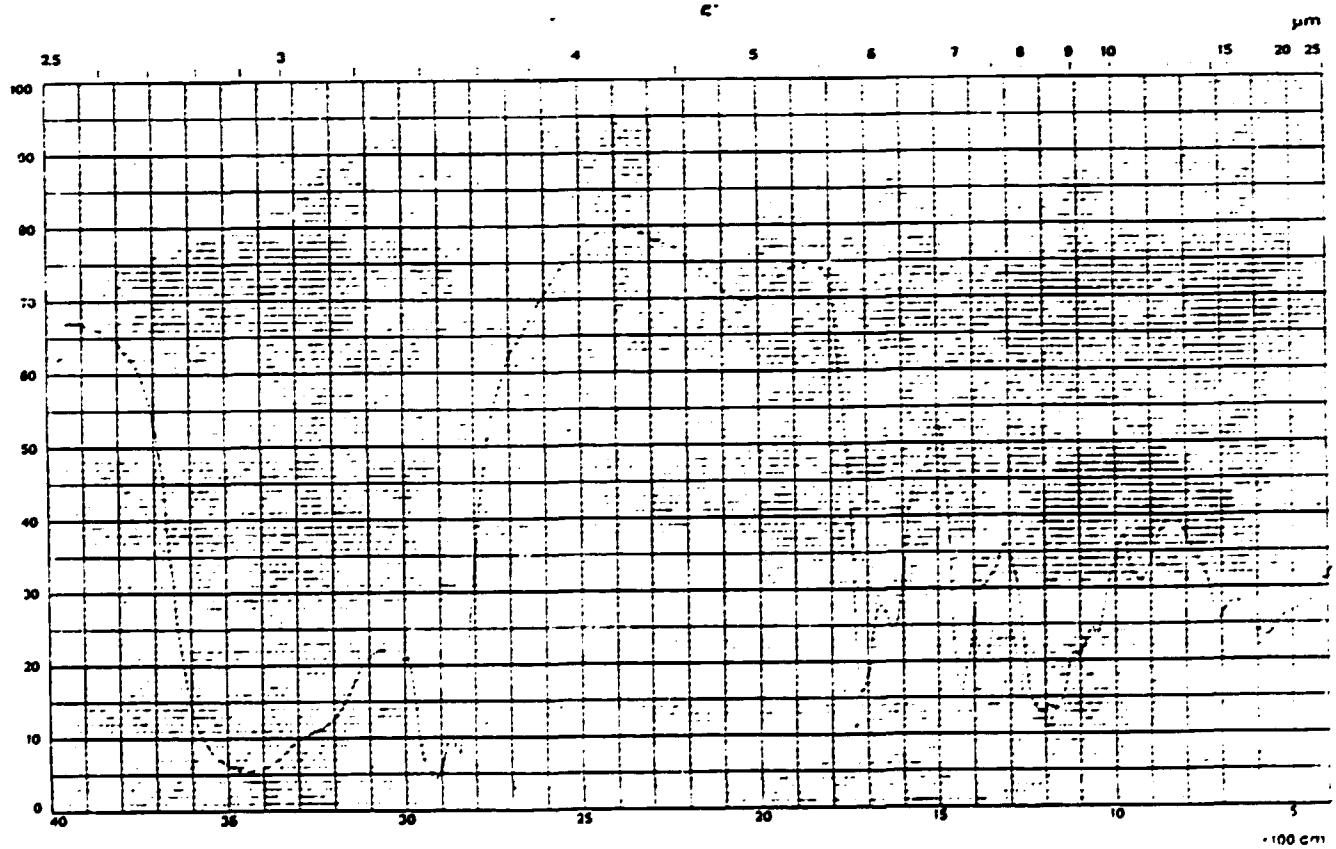

Figure 5.
Infra-red spectrum of fat-liquor 805

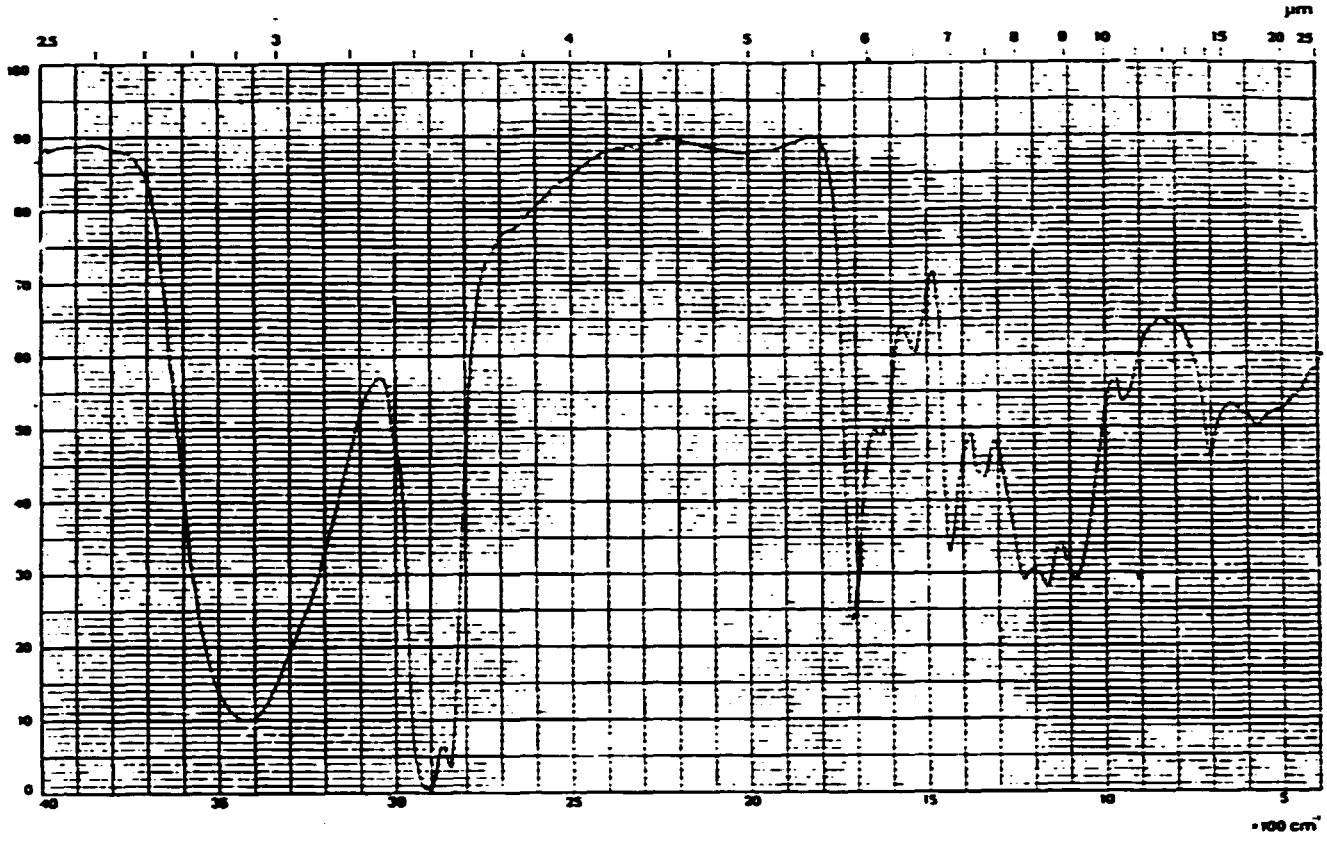

Figure 6.
Infra-red spectrum of a leather-softening fat-liquor

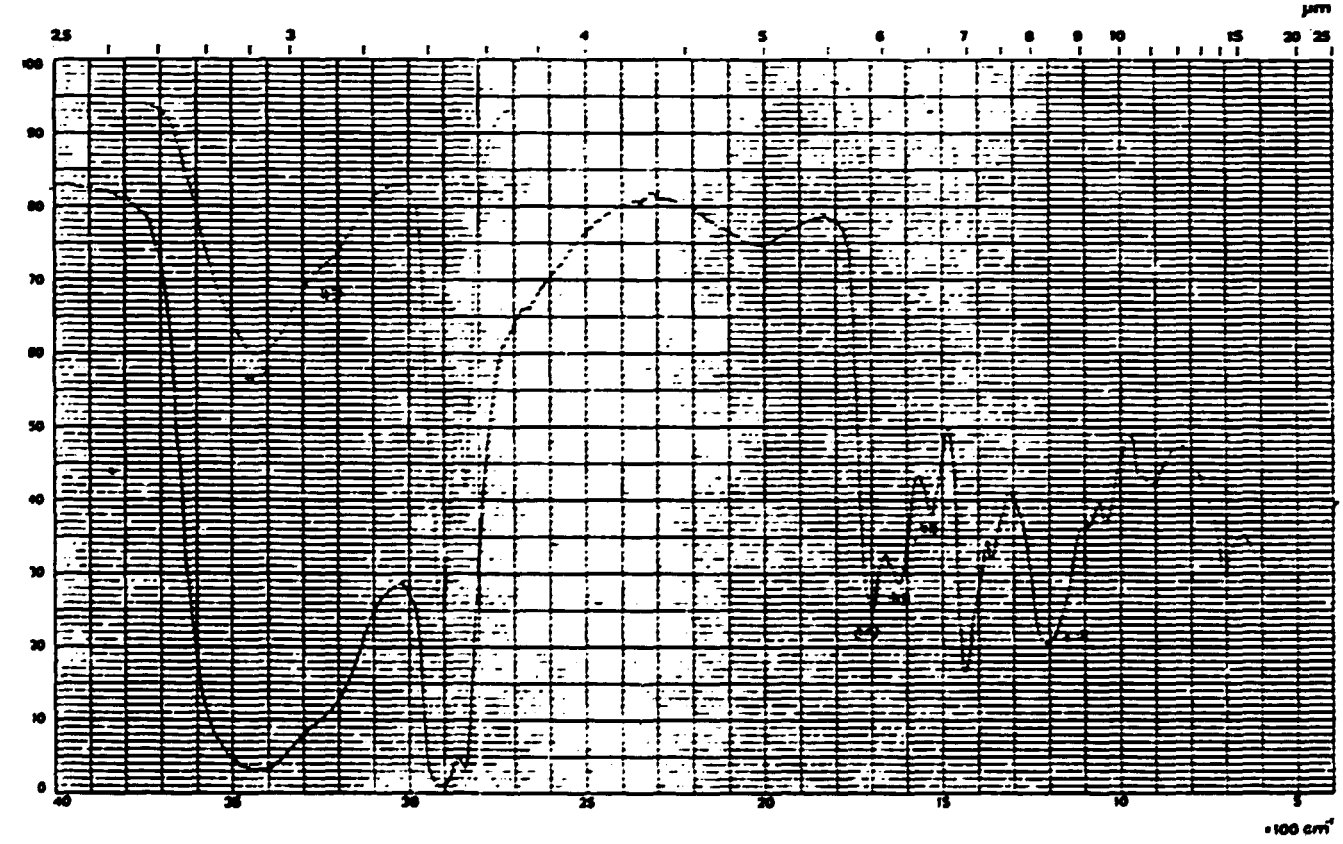

Figure 7.
Infra-red spectrum of a cationic fat-liquor