Meat Science 7 (1982) 299–312

RATE OF FREEZING EFFECT ON THE COLOUR OF FROZEN BEEF LIVER

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(Amended manuscript received: 12 March, 1982)

SUMMARY

One problem that arises when freezing liver in plate freezers is the whitish colour acquired by the liver surface when subjected to high freezing rates.

The purpose of this paper aims to establish optimum operating conditions for freezing beef liver pieces in a minimum time while maintaining an acceptable colour on the surface.

Samples were subjected to different freezing rates and minimum surface freezing time was established in order to obtain an acceptable colour. This was quantified in terms of lightness using a surface colorimeter.

Histological analysis of the samples showed that the size of the ice crystals formed on the contact surface with the coolant is the factor that determines the changes in colour as a result of diffused light reflection phenomena.

On the basis of mathematical heat transfer models with simultaneous change of phase, the minimum characteristic surface freezing time was related to the process operating variables (initial temperature of the liver, coolant temperature, interfacial heat transfer resistance, thickness of the piece), and the optimum freezing conditions were determined, reducing total processing times to a minimum.

NOMENCLATURE

a, m, p, q, r	Numerical constants defined in eqn. (7).
Bi	Biot number; $\mathrm{Bi} = hb/k_0$.
b	Half-thickness.
h	Interfacial heat transfer coefficient ($\mathrm{W/m^2\,K}$).
k_0	Thermal conductivity of unfrozen liver ($\mathrm{W/m\,°C}$).
L	Lightness.

Meat Science 0309-1740/82/0007-0299/$02·75

T	Temperature (°C).
t_7	Characteristic freezing time (min).
t_7°	Characteristic freezing time on the beef liver surface (min).
t_c	Total freezing time (min).
Y_0	Liver water content (wet weight basis).

Greek Symbols

α	Thermal diffusivity of unfrozen liver (m^2/s).
ΔE	Total colour change $\Delta E = ((\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2)^{1/2}$.
η	Dimensionless temperature.
τ_7°	Dimensionless characteristic freezing time on the beef liver surface.

Subscripts

i	Initial.
f	Of the refrigerant.

INTRODUCTION

The surface colour of frozen beef liver is usually considered one of the indices of product quality. Such colour depends, firstly, on the unfrozen liver, which differs according to the type of animal, age, etc., and secondly, on the rate of freezing, which lightens the colour. The choice of the most acceptable colour, however, involves a subjective evaluation for each particular market. In general, pieces with irregular colour find little acceptance.

The determination of optimal colour conditions is an essential requirement in order to increase the rate of production by means of higher freezing rates using plate freezers. In order to obtain these optimal conditions, two important calculations must be made:

(i) To establish maximum surface freezing rates according to the most acceptable colour.
(ii) To convert such information into operating parameters of the freezing process, so as to minimise processing times.

With regards to the first calculation and in relation to the colour of frozen meat products, it is important to take into account the following effects (Kaess, 1961):

(i) Colour changes due to the location, number and size of the ice crystals formed (Guenther & Henrickson, 1962; Jakobsson & Bengtsson, 1973).
(ii) Colour changes (darkening) produced by partial dehydration of surface tissues which causes a higher concentration and oxidation of pigments.

(iii) Changes in colour resulting from 'freeze-burn', producing a greyish-yellow colour in the spongy areas of the tissue. This results from dehydration of frozen tissue during long storage periods in inadequate packaging (Kaess, 1961); (Kaess & Weidemann, 1961, 1962*a*, 1962*b*, 1967*a*, 1967*b*, 1969).

Only the first effect, that connected with freezing rates, will be analysed in the present work. The other two effects depend on time and type of storage of frozen samples.

Referring to the second calculation, it is necessary to establish heat transfer models that simulate freezing of liver in plate freezers. Although, no models have been specifically developed for liver, it is possible to adapt equations previously used for meat (Mascheroni & Calvelo, 1980).

In this work, liver samples were subjected to different freezing rates and the optimum rate was evaluated in terms of the acceptable colour prevailing in the international market. This information was then used in order to obtain better operating conditions in terms of a minimum processing time.

MATERIALS AND METHODS

In order to show the differences in colour detected in industrially frozen livers whether due to the location, number or size of the ice crystals, the following histological determinations were performed.

Histological technique

For histological observations of frozen liver the substitution method at low temperature was used (Cerrella & Zaritzky, 1974). Using this technique, the frozen liver samples were fixed in a Carnoy solution at $-18\,^{\circ}C$ for 4 days.

The fixed material was then subjected to the conventional methods of dehydration, impregnation, and sectioning and staining with haematoxylin and eosin.

The histological analysis of fresh liver tissue was carried out by a conventional substitution technique at room temperature.

Tissue sections from industrially frozen livers and tissue sections obtained under laboratory conditions were studied in order to establish the size and location of ice crystals formed in the liver.

Freezing technique

Cylinder-shaped beef liver samples (5 cm diameter and 3–5 cm in height) cut perpendicularly to the liver surface were used. These were mounted on acrylic sample holders having 4 mm thick walls insulated on the sides and top surfaces, with 4 cm thick expanded polystyrene. The remaining base of the liver sample, with the outer connective capsule (Glisson capsule), rested on a metallic exchanger through which methanol from a Lauda UK 50 DW cryostat, circulated.

Between the surface of the liver and the heat exchanger, slabs of different materials were interposed (acrylic of different thicknesses, polyethylene, 3–9 mm thick corrugated cardboard, etc.) to modify the interfacial heat transfer resistance, thus regulating freezing rates.

Measurements of the thermal histories during freezing were made by means of Copper–Constantan thermocouples placed at the bottom, centre and top of the sample.

In this way, the existing freezing conditions in industrial plate freezers were simulated in the laboratory (the length of the cylinders used being half the thickness of the ones used in industry).

Different experiments were carried out under varying freezing conditions: coolant temperatures between $-25\,^{\circ}C$ and $-40\,^{\circ}C$ and interfacial heat transfer resistances involving values of heat transfer coefficients, h, from 36·4–240 $W/m^2\,K$ were used.

Determination of surface colour

Colorimetric measurements were taken by means of a Hunter Lab model D25 A-3 colorimeter. The equipment was calibrated for lighted section, adequately reduced to the size of the sample used. The frozen pieces were placed in a heat-insulated sample holder to prevent alteration of the surface colour during measurement. Readings proved to be shorter than 3 min in all cases. The values of parameters L, a and b of the original unfrozen liver samples were also measured in order to quantify the changes produced by freezing.

RESULTS

Histological study

Hepatic cells and several lobules with their central and interlobular veins will be observed in fresh liver samples (Fig. 1a).

Histological cuts were obtained from the light and dark areas of industrially frozen liver. A large number of small intracellular crystals with an average size of 26 μm were observed in light areas (Fig. 1b); while big ice crystals (average size = 42 μm) appeared in dark areas (Fig. 1c).

Three laboratory-frozen samples with freezing rates decreasing from 1–3, plus a fresh liver control sample are shown in Fig. 2. In this Figure it is possible to see changes in colour produced by freezing. High freezing rates confer a whitish appearance to the liver surface; this effect decreases at low freezing rate.

Figure 3 shows corresponding histological cuts obtained from the samples shown in Fig. 2. A very quickly frozen sample shows a large amount of smaller sized crystals (15 μm) (Fig. 3a), whilst a slowly frozen sample shows a decreased amount of crystals of a larger size (35 μm) (Fig. 3b).

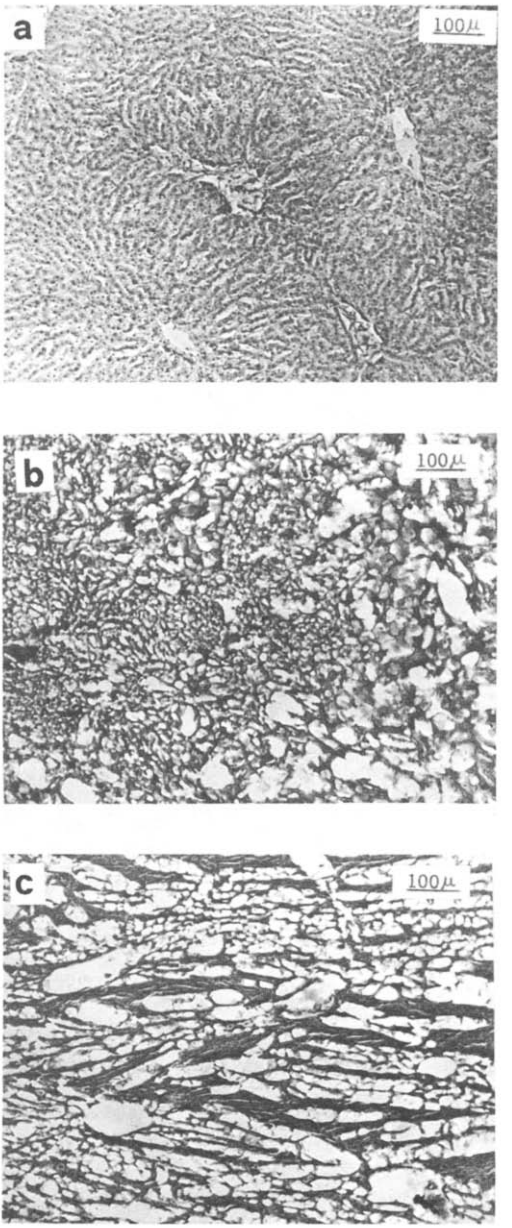

Fig. 1. Histological sections of beef liver corresponding to: (a) unfrozen tissue; (b) light area from the surface of industrially frozen liver; (c) dark area from the surface of industrially frozen liver.

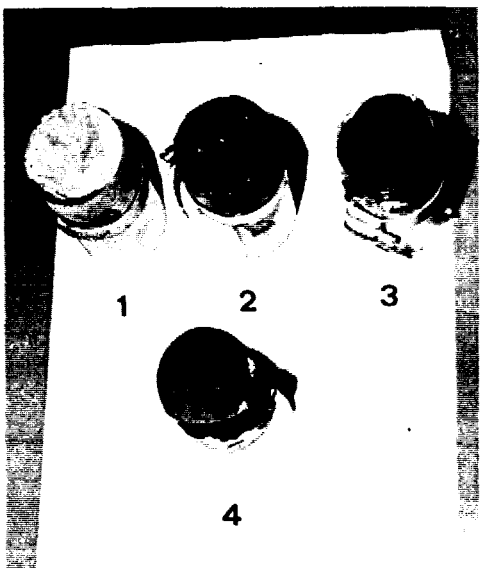

Fig. 2. Effect of freezing rate on the colour of beef liver: Sample 1, $t_7^\circ = 0{\cdot}5$ min; Sample 2, $t_7^\circ = 40$ min; Sample 3, $t_7^\circ = 102$ min; Sample 4, unfrozen liver.

Freezing rate–colour relationship

It can be seen from the above paragraph that it becomes necessary to define a representative parameter of the surface freezing rate.

The characteristic time, t_7, or local freezing time, was adopted as a representative parameter. This is the time which has elapsed at a given point of the piece for the temperature passing from $-1\,^\circ C$ (freezing start) to $-7\,^\circ C$ (freezing of 80 % of the initial water). t_7 correlates satisfactorily with the amount of drip produced by the tissue during thawing (Añón & Calvelo, 1980) and with the morphology adopted by the ice crystals in the cell structure (Bevilacqua *et al.*, 1979).

The lower the t_7, the higher the freezing rate, since the size of the ice crystals is smaller.

Since the characteristic freezing time is a *local* magnitude along an industrially frozen piece, there will be a distribution of t_7 (small values near the surface, increasing towards the centre of the piece). However, the size of the ice crystals on the surface of the liver, and, consequently, its colour will depend exclusively on the t_7 obtained at this point, named as t_7°.

Laboratory experiments for different surface freezing rates (different t_7°) were performed and the parameters L, a and b were measured.

The unfrozen liver colour parameters L_0, a_0 and b_0 were also determined. The experimental results obtained are shown in Table 1.

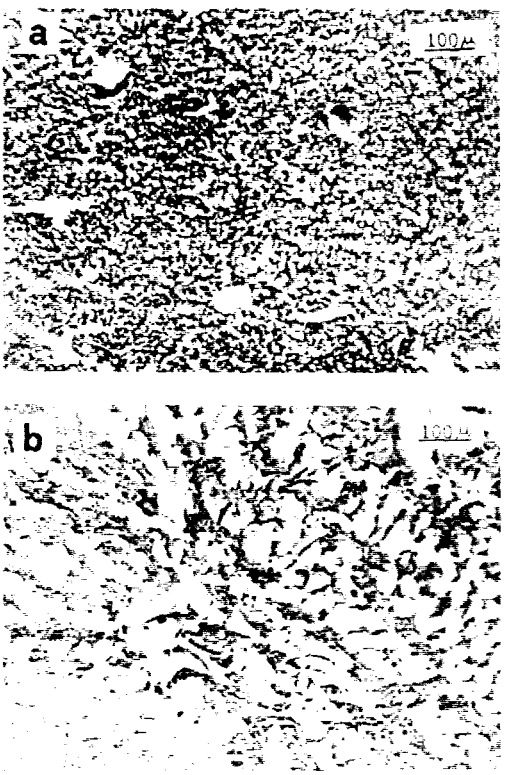

Fig. 3. Histological sections of beef liver frozen under controlled conditions: (a) High freezing rate, $t_7^2 = 14$ min; (b) Slow freezing rate, $t_7^2 = 85$ min.

Values of ΔE (total colour change) defined as:

$$\Delta E = ((\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2)^{1/2} \tag{1}$$

were also included.

Since $\Delta L/\Delta E$ is close to unity, the relationship between colour and the freezing rate was established in terms of ΔL versus t_7° (Fig. 4) (Zaritzky, 1979).

A comparison of colour between frozen livers considered satisfactory by industrial operators with those obtained in the laboratory under different surface freezing rates was carried out. It was possible to establish that the maximum permissible change in the index of lightness in liver due to the effect of freezing is $\Delta L = 12$. According to Fig. 4 this colour corresponds to a characteristic surface freezing time, t_7°, of 90 min.

An acceptable colour will therefore be obtained when:

$$t_7^\circ \geq 90 \text{ min} \tag{2}$$

TABLE 1
CHANGES IN THE COLOUR INDICES WITH THE FREEZING RATE IN LIVER

Unfrozen liver			*Frozen liver*							
L_0	a_0	b_0	t_f^c	L	a	b	ΔL	Δa	Δb	$\Delta E = (\Delta a^2 + \Delta b^2 + \Delta L^2)^{1/2}$	$\Delta L/\Delta E$
23·78	4·58	4·39	0·6	68·16	4·50	11·99	44·38	−0·08	7·51	45·01	0·99
			26·7	41·67	7·62	9·52	17·8	3·04	5·13	18·78	0·95
			48·0	41·99	7·08	8·86	18·2	2·5	4·47	18·90	0·96
			1·2	69·67	3·42	11·57	45·89	−1·16	7·18	46·46	0·99
			40·0	42·78	6·50	8·50	19·0	1·92	4·11	19·53	0·97
			109·0	36·3	8·79	9·85	12·52	4·21	5·46	14·29	0·88
25·28	1·23	3·27	39·5	42·92	7·28	12·31	17·34	6·05	9·04	20·46	0·85
			23·7	44·40	7·17	11·00	19·12	5·94	7·73	21·46	0·89
			28·8	45·12	8·42	12·69	19·84	7·19	9·42	23·10	0·86
28·04	4·65	4·84	4·5	56·24	4·37	12·52	28·20	−0.28	7·68	29·22	0·96
			28·1	50·22	4·73	10·98	22·18	0·08	6·14	23·01	0·97
27·14	8·93	10·23	102·5	39·08	7·66	8·89	11·94	−1·27	−1·34	12·08	0·99
			115·5	41·19	7·71	8·69	14·05	−1·22	−1·54	14·21	0·99
			80·0	41·78	9·32	9·46	14·64	0·39	−0·77	14·66	0·99
32·10	7·06	3·63	5·2	56·79	5·09	7·58	24·69	1·96	3·95	25·08	0·98
			68·0	44·89	7·62	9·88	12·79	0·55	6·25	14·25	0·90
			121·0	44·52	6·49	11·88	12·29	−0·55	8·27	14·82	0·83
			68·1	48·77	6·32	10·00	16·67	−0·74	6·37	17·86	0·93
			22·0	54·18	5·51	10·9	22·08	−1·55	7·27	23·29	0·95
			10·6	40·02	8·07	10·2	7·90	1·01	6·57	10·32	0·76
31·57	8·00	3·37	7·0	54·24	6·29	11·90	22·67	−1·71	8·53	24·28	0·93
			54·25	49·85	6·21	11·10	18·2	−1·79	7·73	19·85	0·92
30·02	7·75	7·03	24·2	50·71	6·65	11·40	20·69	−1·10	4·37	21·17	0·98

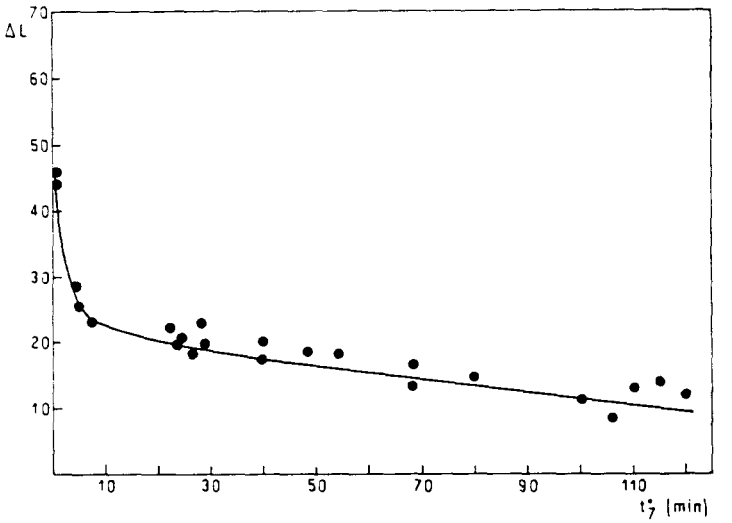

Fig. 4. Lightness change (ΔL) as a function of the surface characteristic freezing time (t_7°) for beef liver.

Relationship between minimum t_7° and operating variables

Several combinations of operating variables (T_f, T_i, h, L, etc.) make it possible to fulfill $t_7^\circ \geq 90$ min. In order to relate this criterion to the operating variables in industrial freezers, a mathematical heat transfer model with simultaneous change of phase was used.

Mascheroni and Calvelo (1980) developed a model for freezing beef which can be adapted to liver by using different thermal properties required for liver freezing. This model makes it possible to obtain a relationship between t_7° and the total freezing time, t_c. t_c is usually defined as the interval required to change the temperature from the uniform initial one, T_i, to $-18\,^\circ$C in the centre.

This model analyses heat transfer with simultaneous change of phase of a piece $2b$ thickness with an initial uniform temperature, T_i, and frozen unidirectionally with a coolant at a T_f temperature. In the interphase between the sample and the coolant, the existence of a heat transfer resistance characterised by a heat transfer coefficient, h, is found.

The mathematical model was solved using an IBM/360 computer obtaining numerical functions of the type:

$$\tau_7^\circ = \tau_7^\circ(T_i, T_f, \mathrm{Bi}) \tag{3}$$

where the characteristic dimensionless time on the surface τ_7° has been defined as:

$$\tau_7^\circ = \alpha_0 t_7^\circ / b^2 \tag{4}$$

and the Biot number as:

$$\mathrm{Bi} = hb/k_0 \tag{5}$$

where α_0 and k_0 are thermal diffusivity and thermal conductivity, respectively, of the unfrozen liver ($\alpha_0 = 1{\cdot}258 \,.\, 10^{-7}\,m^2/s$; $k_0 = 0{\cdot}49\,W/m\,°C$).

The variation in the thermal conductivity of frozen liver with the temperature was established in a previous work (Barrera & Zaritzky, 1981) and used in the cited model.

According to the numerical model τ_7° were plotted in terms of T_f and Biot number for an initial temperature of 25 °C (Fig. 5). It can be seen that by increasing Bi (lower thermal resistance), τ_7° decreases. The same effect is obtained by lowering the coolant temperature T_f.

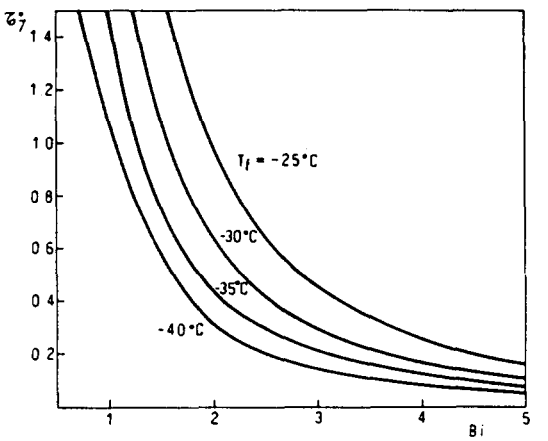

Fig. 5. Dimensionless characteristic freezing time on the beef liver surface t_7° versus Biot number (Bi) for different temperatures of the refrigerant (T_f) and initial temperature ($T_i = 25\,°C$).

In order to obtain an acceptable colour on the surface of frozen liver while freezing it at maximum rate, t_7° must equal 90 min.

$$t_7^\circ = 90\,\text{min} \tag{6}$$

This value was introduced into equation (4) and the τ_7° corresponding to each b was calculated. Then, from Fig. 5, the limits for operating conditions T_i, T_f, Bi were obtained, which in turn, fulfil eqn. (6).

The acceptable isocolour curves of Fig. 6 were thus obtained. These curves were designed for initial liver temperature of 3 °C and 25 °C and for b values of 3–6 cm.

Figure 6 allows us to determine from a plot of T_f against Bi, the operating conditions giving a satisfactory colour for a liver piece of half-thickness, b. Thus, the colours from the left of the isocolour curve, will be acceptable, since they correspond to lower values of freezing rates than the reference limit; however, this will imply a lower production rate.

Limit isocolour curves ensure the same acceptable colour of the liver surface for different combinations of operating variables, although it will not imply the same total freezing time.

These freezing times vary along the curves, and the determination of the most suitable processing conditions must be obtained by minimising the corresponding total freezing times.

With regard to this, the numerical model used allows us to establish a relationship between total freezing time, t_c, and the operating variables involved, as:

$$t_c = \frac{ab^2}{60\alpha_0} \mathrm{Bi}^{-m} \eta_f^{-p\eta_i} Y_0^{-r} \tag{7}$$

where $\eta_f = -T_f/273{\cdot}16$; $\eta_i = T_i/273{\cdot}16$, Y_0 is the moisture content of the liver ($Y_0 = 0{\cdot}74$); $a = 0{\cdot}0454$; $m = 0{\cdot}2022$; $p = 1{\cdot}3557$; $q = 1{\cdot}2298$ and $r = 2{\cdot}0778$.

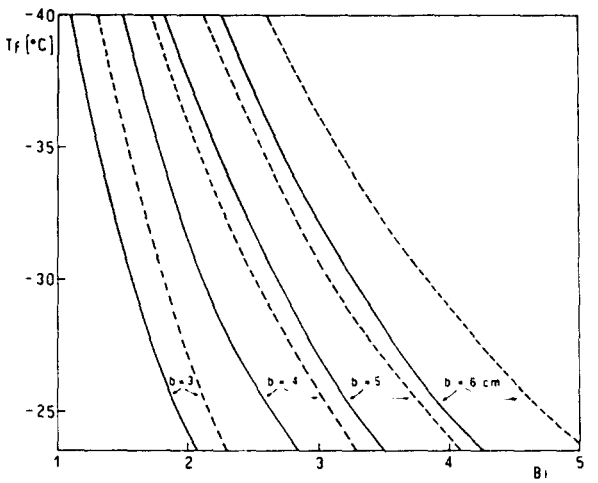

Fig. 6. Processing conditions leading to an acceptable beef liver colouring. T_i: ——. 3 °C; – – –, 25 °C.

The t_c values for the different combinations which produce the same colour were calculated by introducing into eqn. (7) the isocolour conditions from Fig. 6. These t_c values were plotted in terms of T_f for different b and T_i values as shown in Fig. 7. The Biot number does not appear to be explicit because it is automatically determined when the eqns (6) and (3) are fulfilled simultaneously.

It is more convenient to use low coolant temperatures and high interfacial heat resistances (low Bi number) in order to minimise total freezing time and to obtain acceptable colour on the surface.

The effect of the initial temperature, though small, indicates that it is convenient to precool the piece to be frozen.

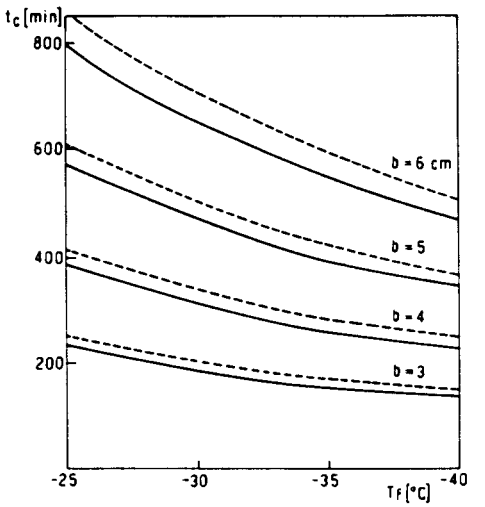

Fig. 7. Total freezing time (t_c) versus temperature of the refrigerant (T_f) for different values of half-thickness (b) and initial temperature (T_i). ——, 3 °C; – – –, 25 °C.

Colour regeneration by recrystallisation

Recrystallisation is a phenomenon in which an increase in the average ice crystal size is produced. It occurs when frozen products are temporarily subjected to an increase in temperature. In this way, the small ice crystals disappear leaving only the larger ones, since a state of minimum surface energy has to be achieved. Taking this into account, a reversion of the light colour of the liver surface by recrystallisation was analysed.

To achieve regeneration of the liver colour by recrystallisation two surface heat treatments were used:

(a) A hot air current ($v = 4{\cdot}5$ m/sec and $T = 75$ °C) was passed over the frozen liver surface until it reached a temperature of -1 °C. The sample was then placed in a chamber at -18 °C until the temperature was homogeneous throughout the sample.

(b) Liver pieces were heated with a radiant source of heat ($T = 900$ °C). The samples were placed at 20 cm in between until the liver surface reached -1 °C and then placed at -18 °C.

In both treatments the time required for raising the surface temperature from -7 °C to -1 °C was measured. Values of 4·5 min for the first and 6 min for the second were recorded (4 cm thick samples).

In every case highly satisfactory colours were obtained after applying the above mentioned heat treatment.

The significance of the use of recrystallisation, for the reduction of the non-

uniform colour produced by the deficient thermal contact during the freezing process was also determined.

Experiments were carried out in which liver samples were frozen with different interfacial heat resistances, as shown in Fig. 8(a). Here, one half was frozen with a $t_7^\circ = 42$ min, while the lighter one involved a $t_7^\circ = 0{\cdot}8$ min.

In Fig. 8(b), which shows the same sample after a surface heat treatment, it can be seen that a recrystallisation process tends to make the colour differences uniform.

In every case, histological determinations were performed, before and after the application of surface heat treatments. Increase in the crystal size from 4–33 μm due to recrystallisation was observed. It should be noted that treatment (b), which uses a source of radiant heat produced better results than treatment (a).

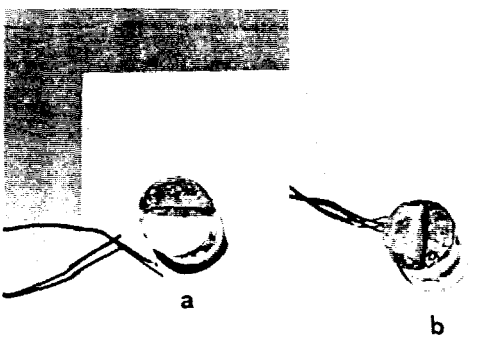

Fig. 8. Effect of the surface heat treatment on the regeneration of the liver colour: (a) Liver sample frozen with different interfacial heat resistances; (b) The same sample after surface heat treatment.

CONCLUSIONS

The results described made it possible to deduce the following conclusions:

(a) The lighter colour observed in frozen liver is caused by the small ice crystals existing on its surface.

(b) Due to the fact that crystal size is a function of a corresponding freezing rate, it is possible to establish a relationship between an acceptable colour and a given freezing rate, quantified by surface freezing time, t_7° (Fig. 4). For $t_7^\circ \geq 90$ min, the colour thus obtained is acceptable.

(c) Based on the t_7° necessary to obtain a good colour, limit operating conditions were established for industrial freezers, according to Fig. 6.

(d) Total freezing times, t_c, for acceptable surface colour were calculated. These t_c values are shown in Fig. 7, which also shows which are the conditions that help to minimise them. So it is convenient to work with low coolant temperatures and high interfacial heat transfer resistances. The effect of initial temperature, though small, indicates that it is useful to pre-cool the sample to be frozen.

(e) Recrystallisation appears to be an adequate procedure in those cases in which higher freezing rates ($t_7^\circ \geq 90$ min) ought to be used. Using a brief additional heat treatment, a highly acceptable colour will be obtained.

(f) A recrystallisation procedure seems to be suitable in order to obtain a uniform colour in spotted pieces.

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