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CONTENTS

AN OPTICAL METHOD TO STUDY THE KINETICS OF CLEANING MILK DEPOSITS BY SODIUM HYDROXIDE

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ABSTRACT

An optical sensor was devised to observe cleaning kinetics of heat exchange surfaces fouled by milk and to study the influence of some parameters on them.

The sensor works by sensing the attenuation of incident light by the suspension of deposits which are removed by the cleaning solution.

The cleaning is carried out without recycling the cleaning solution. The on-line collected numerical data are converted into concentration values by the use of an empirical correlation based on samples of freeze dried deposits diluted with soda solutions. The cleaning kinetics and the weight of removed fouled material are computed for each experiment by integrating the concentration versus time curve.

Over 20 experiments, carried out on a plate milk pasteurizer have established the validity of the method. The kinetics are interpreted as initially zero order, but first order at the end of the process.

INTRODUCTION

In any food industry cleaning is needed as well as systematic disinfection of equipment. Some processes such as thermal treatment or the flow of sticky substance cause particularly severe fouling, and then cleaning is difficult and expensive.

The control of cleaning operations is generally automatic using Cleaning-In-Place units. But if cleaning conditions (temperature, concentration and composition of the cleaning solution) are more or less chosen by experiment, excess cleaning time is almost always used because no parameter is directly measured on site to allow one to follow the progress of cleaning.

The mechanisms and kinetics of cleaning have been very little studied, the best known works being those by Jennings (1963) and Schlüssler (1976). Their results essentially come from the laboratory

[1] Research conducted during a Doctor-Engineer Thesis sponsored by the Food Engineering Department of ENSIA-Massy (Prof. B. Guerin)

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cleaning of small samples, using periodic measurement of the residual radioactivity of radioactively fouled surfaces.

Analysis of the works of Ruiz *et al.* (1975) who studied the optical characterization of small quantities of milk in different cleaning solutions, and our experience with optical measurement of material in suspension led us to propose an optical sensor which would permit on line measurement of the removed deposits while a fouled system is being cleaned. We describe the functioning of this sensor and explain the particular problems we dealt with to calibrate it. Lastly, we show how it can be used for cleaning kinetics studies of a plate heat exchanger used for milk pasteurization.

MATERIALS AND METHODS

Description of the Optical Sensor

Corrieu *et al.* (1980) developed a sensor permitting on line measurement of the turbidity of a suspension flowing through a pipe by the variation of the light intensity of a beam passing through the suspension. The sensor consists of a one inch diameter glass tube inserted in a stainless steel protective system (Fig. 1). Two diametrically opposite optical fibers are placed on the glass tube perpendicular to the suspension flow. One fiber transmits a white light beam into the suspension, the other transmits the attenuated beam which has crossed the suspen-

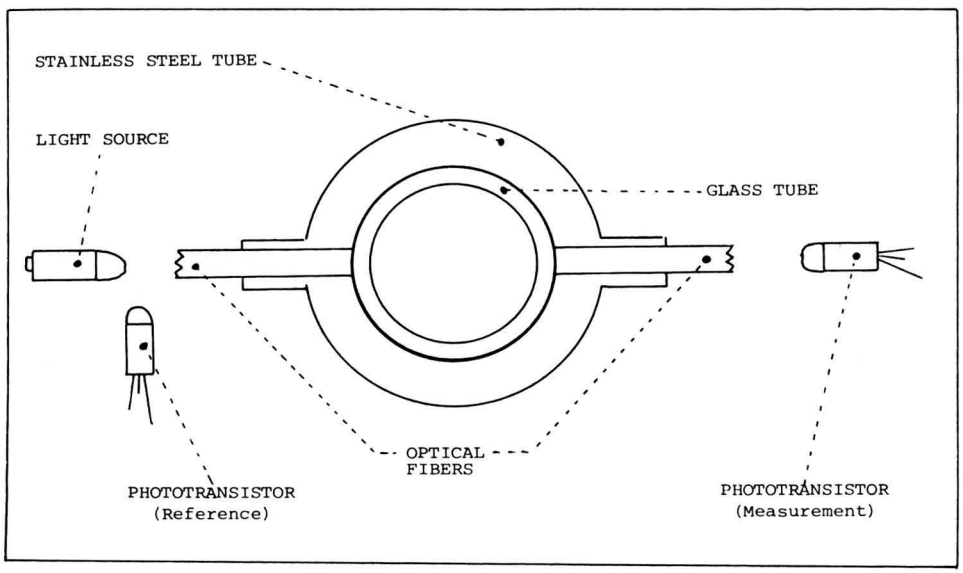

FIG. 1 SCHEMATIC REPRESENTATION OF THE OPTICAL MEASURING CELL

sion to a phototransistor. By using two optical fibers we can isolate electronic part of the sensor from the measurement cell and thus not take the temperature of the analysed medium into account.

The input current created by the phototransistor is amplified and converted into ouput voltage. Two phototransistors are used, one measuring the incident light, the other measuring the attenuated light. By using this technique, the ageing of the light source need not be taken into account. The amplifiers provide on output voltage which is inversely proportional to the input current. Therefore, the more turbid the suspension the weaker the created current and the higher the measured voltage.

We showed that this sensor is sensitive over a concentration range varying from whole milk down to 10^{-4} dilution of whole milk.

Calibration of the Optical Sensor

Because calibration of the optical sensor is difficult, a two step calibration procedure was developed. To avoid having to recalibrate completely whenever there was need to replace a defective light source, we did not correlate the deposit concentration directly with the output voltage of the sensor, but with optical density measured with a spectrophotometer. This measurement has the advantage of being totally independent of the sensor, and if the light source is changed only calibration of the electrical signal in terms of the corresponding optical density is required. The latter is measured at a wavelength of 600 nm where the spectra of milk and of suspensions of deposit in sodium hydroxide are flat. This avoids measuring absorption caused by compounds whose nature and quantity would not be constant for all deposits studied. Moreover, at 600nm the yellow colouring of the samples is avoided.

The first step of the calibration consists in correlating the deposit concentration in the cleaning solution with optical density, and with sodium hydroxide concentration; since it was noticed that for equal deposit concentration the lower the sodium hydroxide concentraion, the higher the optical density. This phenomenon was also observed by Ruiz *et al.* (1975) at different concentrations of milk and sodium hydroxide.

It is difficult to obtain samples of deposit in suspension in sodium hydroxide solutions whose mass is perfectly known. We initially collected deposit samples automatically during cleaning experiments; but it was difficult to measure the exact quantity of suspended dry matter in such samples because the proportion of sodium hydroxide changing into sodium carbonate when the sample is put into the oven is not known. One possibly could use milk instead of deposit suspension but the regression coefficients of the calibration relation differ from those

obtained with deposit. Finally, we used freeze dried moist fresh deposits. Thus samples were prepared and their concentrations in sodium hydroxide and deposit were perfectly known.

The method of preparation is: freeze dried deposits are added to sodium hydroxide in a 100 ml vessel where they are stirred at a constant temperature of 80°C. Since the mixing of deposit with sodium hydroxide is not immediate and varies with the sodium hydroxide concentration, the optical density ultimately reaches a maximum value for each sodium hydroxide concentration.

The weight of the freeze dried deposit placed in each sample is chosen so that for sodium hydroxide concentration ranging from 0.4 to 10% the values of optical density are always less than to 1. For each value of sodium hydroxide concentration the optical density measured is proportional to the deposit concentration of the sample in agreement with the Beers-Lambert law (Fig. 2). The correlation coefficients of the linear regression vary from 0.9908 to 0.9994. The slopes of each straight lines are a logarithmic function of sodium hydroxide concentration (Fig. 3).

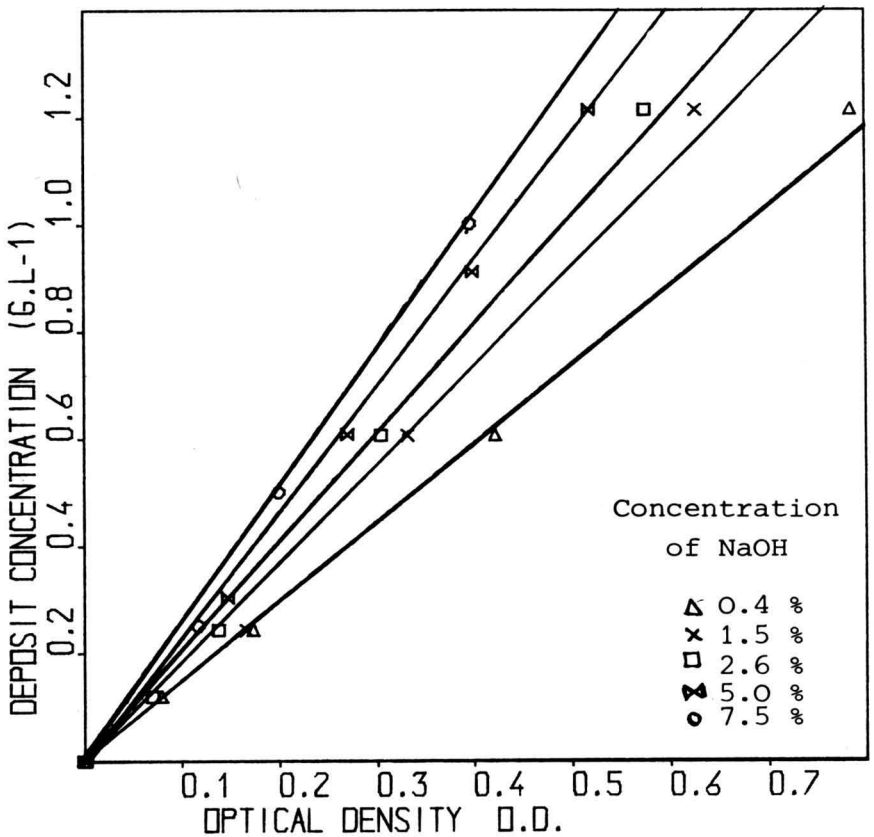

FIG. 2 VERIFICATION OF THE BEER-LAMBERT LAW FOR THE DEPOSIT IN SUSPENSION AS A FUNCTION OF SODIUM HYDROXIDE CONCENTRATION

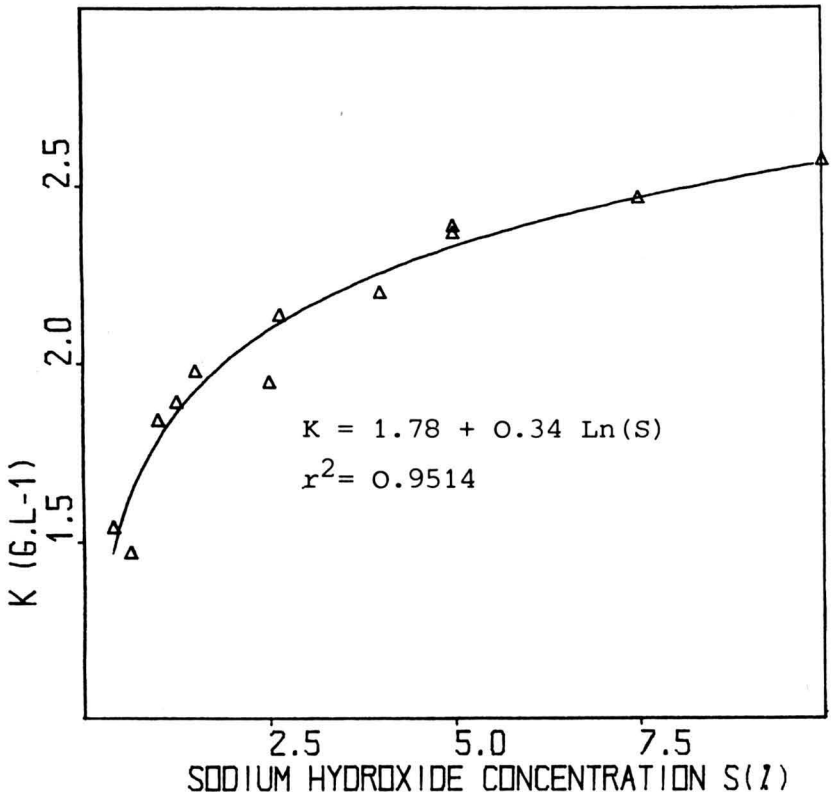

FIG. 3 EFFECT OF SODIUM HYDROXIDE ON THE COEFFICIENT OF PROPORTIONALITY BETWEEN THE DEPOSIT CONCENTRATION AND THE OPTICAL DENSITY

The second step of the calibration consists in converting the output voltage of the optical sensor into an equivalent optical density. The advantage of calibration in two steps is that more easily obtained calibrated samples can be used for the second step. If we consider the optical properties of the parts of the sensor (light source, optical fibers, phototransistors) the ideal replacement substance must have a spectrum corresponding to that of deposit mixed with sodium hydroxide and must follow the Beers-Lambert law. Milk meets these two conditions. Figure 4 shows the relationship between the optical density and the output voltage established by circulating different dilutions of homogenized milk through the optical sensor.

Cleaning of the Fouled System

In our study the fouled system was a plate milk pasteurizer. The weight of deposits obtained during the pasteurization of whole milk varied from 50 to 400 g/m^2. (Lalande 1981). The cleaning is performed in turbulent flow without recycling the solution.

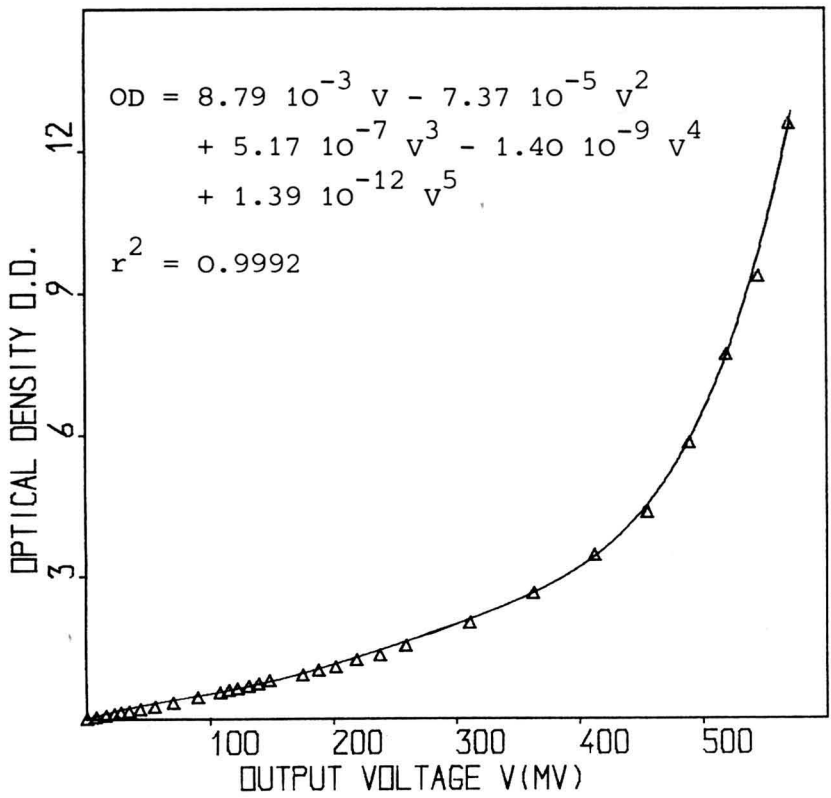

FIG. 4 CALIBRATION OF THE OPTICAL SENSOR INTO EQUIVALENT OPTICAL DENSITY USING MILK

The experimental setup (Fig. 5) consists of two storage tanks, one of them containing water purified by reverse osmosis and the other sodium hydroxide solution. These tanks feed, by means of a three way pneumatic valve, a pump whose speed is automatically regulated so as to maintain a constant value of the measured flow rate. This pumped fluid is heated by the heat exchanger which constitutes the fouled system. The outlet temperature of the pasteurizer is automatically regulated. The exiting solution flows through the optical sensor and a resistivity gauge which measures its sodium hydroxide concentration by means of an empirical calibration. The system is started with water until it reaches preselected operating values of the parameters (temperature, flow rate), at which point it is switched over to sodium hydroxide solution by activating the three way valve.

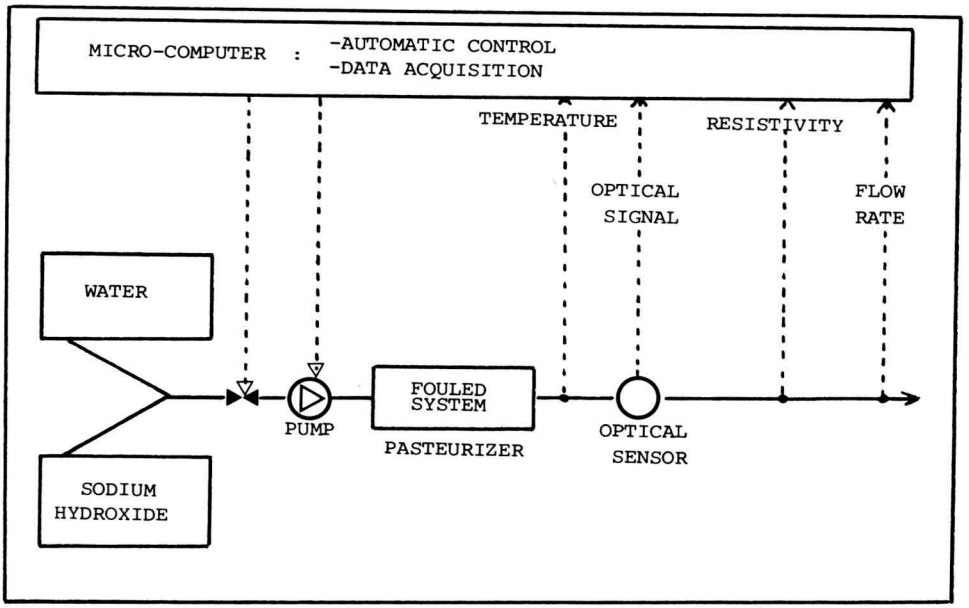

FIG. 5 DIAGRAM OF THE EXPERIMENTAL DEVICE

The cleaning process is entirely controlled by a microcomputer which controls the automatic cleaning of the system and collects data in real time (flow rate, temperature, optical signal, resistivity). The frequency at which data are collected gradually decreases from one to ten seconds between the beginning and the end of the cleaning process. Figure 6 shows the progressive change with time of the optical sensor output voltage during three cleaning experiments which represent the various types of behavior observed. The results are stored on a magnetic disc so as to be used later. Zero time does not correspond to the moment when the pump is fed with sodium hydroxide, but is shifted, with a safety margin, to account for the time needed for the solution to reach the fouled system.

Data Processing

In most literature on this subject, cleaning kinetics are established from the off line measurement of the remaining deposit mass to be cleaned (e.g. radioactive counting by Jennings (1959)). The use of an optical sensor linked to nonrecycled cleaning solution enables us to measure the reaction rate directly and on line. Thus, this method is particularly useful for establishing kinetics.

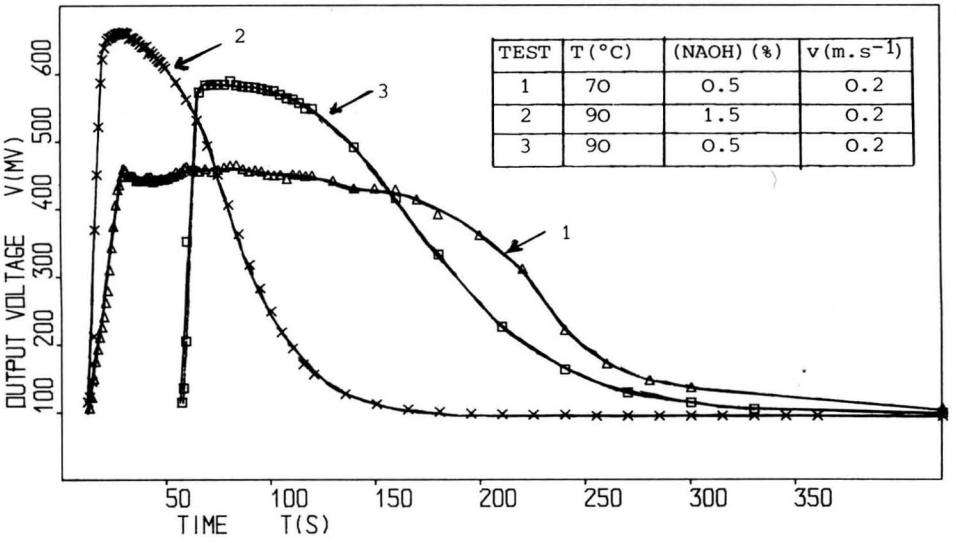

FIG. 6 ELECTRICAL SIGNAL GIVEN BY THE OPTICAL SENSOR DURING THE CLEANING PROCESS

Thanks to the previously established correlations, the deposit concentration of the cleaning solution coming out of the fouled system is evaluated in real time from the signals provided by the sensor. To obtain the quantity of deposit exiting per unit time, these results are multiplied by the sodium hydroxide solution flow rate.

This provides the cleaning reaction rate as a function of time. Numerical integration of these rate curves provides the total mass of the deposit removed since the beginning of the cleaning process. It also allows us to represent the kinetics in a traditional way.

RESULTS AND DISCUSSION

Use of the Optical Sensor for the Cleaning of a Plate Milk Pasteurizer

It is obvious that there is a great difference between the conditions of preparation of the samples used to calibrate the sensor and those resulting from cleaning the pasteurizer (turbulence, residence time in the system, state of deposit). Nevertheless, as shown in Fig. 7, there is a satisfactory correlation between the initial weight of dry deposit and the weight calculated using the optical method. The relative dispersion of the results is caused more by the method of weighing the deposit, than by the optical measurement. In fact, the dry weights obtained

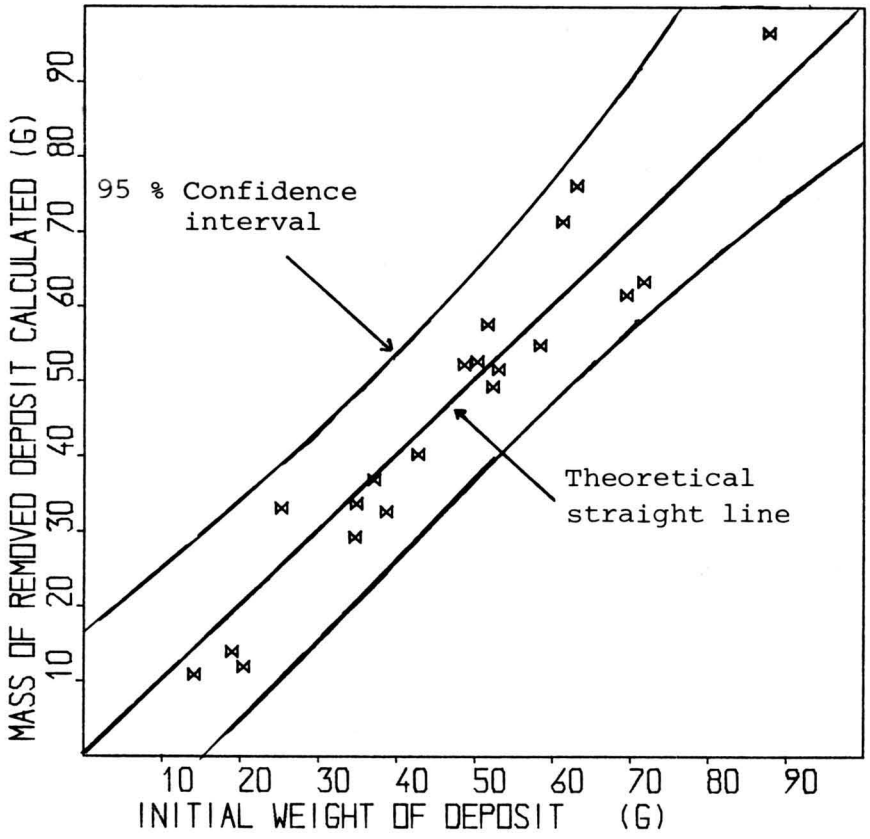

FIG. 7 DIAGRAM SHOWING THE ABILITY OF THE OPTICAL SENSOR TO INTERPRET THE CLEANING OF A FOULED SYSTEM

were determined by weighing a moist deposit and converting it into dry weight, using a relation which allowed for an error margin of five grams.

It appears therefore that the use of the optical sensor for the calculation of the mass of the removed deposit during cleaning is satisfactory.

An Attempt to Interpret the Kinetics

For a first order reaction, the reaction rate is proportional to the total mass of deposit which is still to be cleaned, and thus, decreases exponentially with time. For a zero order, the reaction rate depends on the deposit surface in contact with the cleaning solution, and is constant versus time.

For each test we plotted the cleaning rate as a function of time. Figure 9 shows three curves which are typical of the kinetics observed. The following conclusions can be drawn from these curves: (1) The Cleaning of milk deposits by sodium hydroxide solution is a rapid process lasting only a few minutes. Some cumulative removal curves are shown in Fig. 8. (2) The length of time required to reach the maximum cleaning rate varies as the test conditions vary. Two hypotheses are proposed to explain this cleaning stage. On the one hand, due to residence time distribution the sodium hydroxide front spreads during the ten seconds which pass before the solution reaches the fouled system. We can thus suppose that the first grams of deposit are removed with a variable sodium hydroxide concentration, which is less than the concentration in the storage tank. On the other hand, the reaction between sodium hydroxide and the deposit may not be immediate. Schlüssler (1976) described cleaning as a several step process which a period of penetration of the deposit by sodium

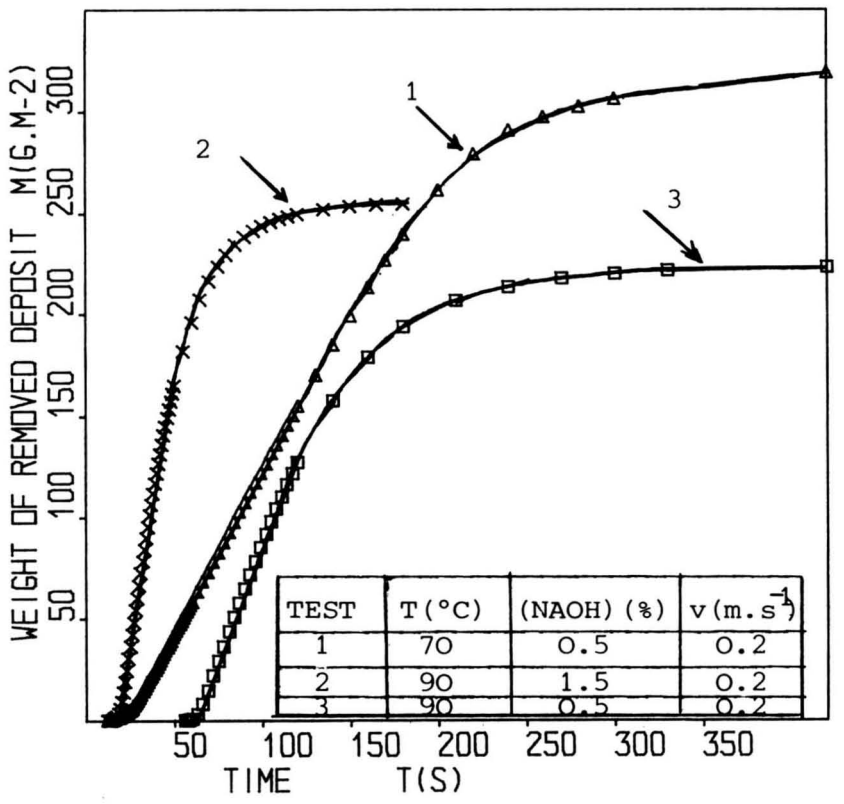

FIG. 8 CLEANING CURVES AS A FUNCTION OF TIME FOR DIFFERENT EXPERIMENTAL CONDITIONS

hydroxide and a period during which the deposit goes into suspension. (3) As soon as the maximal rate is reached two different types of behavior can be observed (Fig. 9). They will be named type one and type two. For type one curves, the cleaning rate remains constant during a certain period of time which is in agreement with a zero order reaction. For the type two curves, this rate decreases very rapidly but the reaction is not first order for the curve of the logarithm of the reaction rate as a function of time is not linear (Fig. 10).

However, if we take into account the experimental fact that the deposits are not uniformly spread on the whole surface to be cleaned, the behavior observed is in agreement with a zero order reaction. In fact, we performed a numerical simulation of the progressive change in cleaning rate for a zero order reaction in a system where the depth of deposit varied linearly. The calculations show that after the constant rate stage, the cleaning rate decreases linearly as soon as the input or output end of the fouled system is clean. Thus zero order kinetics can be experimentally justified even when the observed rate decreases.

To further confirm initial kinetics of zero order we calculated the value of the maximal initial cleaning rate for paired tests performed at constant temperature and sodium hydroxide concentrations, in which the initial weight of deposit was varied. The results (Table 1) show that the maximum initial reaction rate is indepedent of the initial weight of deposit. Therefore, they confirmed a zero order reaction. (4) Lastly, in all cases, at the end of cleaning the rate decreases exponentially with time, as the logarithmic curves in Fig. 10 show. This corresponds to a first order reaction.

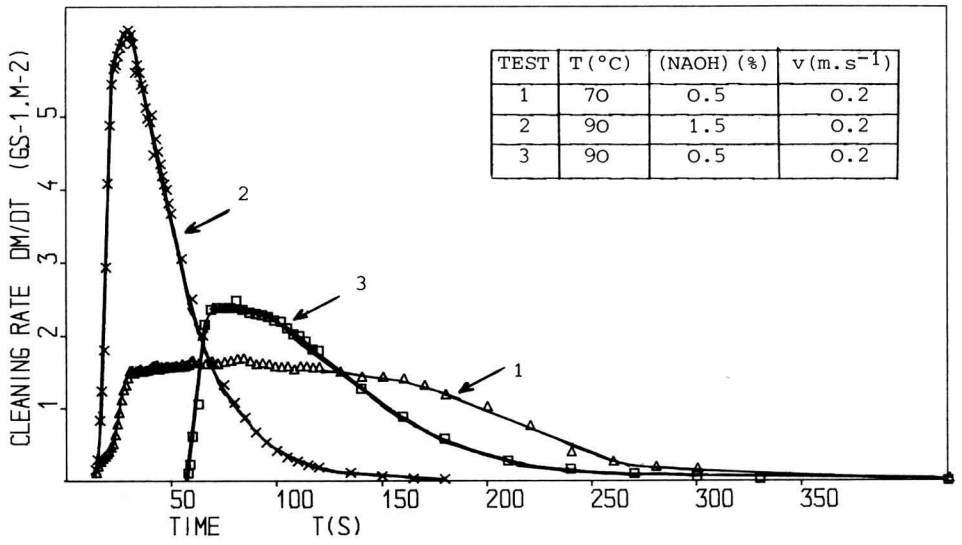

FIG. 9 CLEANING KINETICS FOR DIFFERENT EXPERIMENTAL CONDITIONS

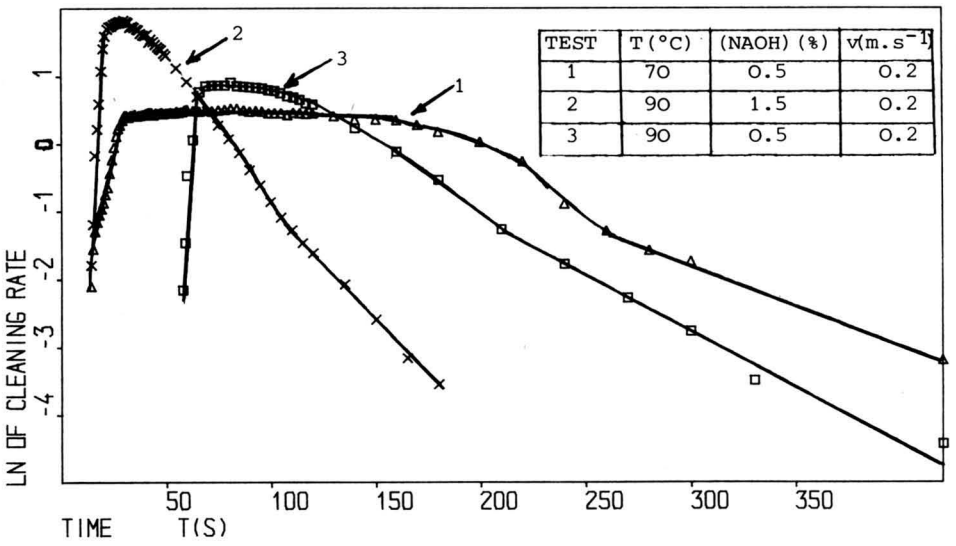

FIG. 10 LOGARITHMIC REPRESENTATION OF CLEANING KINETICS

Table 1. Data showing a zero order reaction at the beginning of the cleaning

Temperature C°	Concentration of Sodium Hydroxide %	Initial Weight of Deposit $G.M^{-2}$	Maximal Initial Reaction Rate $G.S^{-1}.M^{-2}$
71	4.7	72	4.5 ± 0.4
70	4.8	122	4.6 ± 0.4
85	4.7	82	7.1 ± 0.7
85	4.9	115	7.2 ± 0.7
91	5.1	112	9.3 ± 0.8
90	5.1	159	8.6 ± 0.7

To sum up we have observed that after a transient rapid increase in cleaning rate, the initial cleaning kinetics observed can be explained by a zero order reaction, the reaction rate depending on the surface of deposit still in contact with the cleaning solution. The latter part of cleaning can then be explained by a first order reaction, in agreement with the results observed by Jennings (1963) and Schlüssler (1976). Physical interpretations of these zero and first order reactions have not been developed.

CONCLUSION

A properly calibrated optical sensor permitted on line monitoring of the cleaning of a plate heat exchanger used for milk pasteurization. Because of the method of calibration, a new calibration depending on the substance treated would be required if it was to be used in other food industries.

The observed kinetics lead us to interpret the phenomenon in a way different from the literature on this subject, which indicate that cleaning reactions are first order. It appears that in our case, the cleaning reaction is initially a zero order and then, is first order.

The observed kinetics permit one to study the influence of different parameters on the cleaning rate (temperature, concentration, nature and flow rate of the cleaning solution). This work is now being carried on.

The pattern of cleaning kinetics as measured by the direct use of the optical sensor in industrial cleaning processes would allow better control of cleaning operations.

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RESPIRATION ACTIVITY OF SHELLED CORN

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ABSTRACT

To be able to minimize losses in terms of quantity and quality during storage time, investigations to determine the relations between respiration of shelled corn and moisture content and temperature were carried out. The main part of this paper consists of a description of a quick method to determine the amount of carbon dioxide produced and discusses the results evaluated by using this method. These results were checked by comparing them with respiration data evaluated with 0.6 m^3 bins which are also briefly discussed.

INTRODUCTION

Shelled corn (maize), like other cereals, is a living thing in and on which biological processes take place during storage. One of these processes is respiration. The heat and moisture produced by the respiration of cereals has an adverse effect on their storage stability. On the one hand, the heat produced in the respiration process causes, because of the low thermal conductivity (Scherer 1979), a rise in temperature (spontaneous heating) with associated germ damage and increased biological activity. On the other hand, the moisture also produced promotes deterioration of the stored goods by mould growth. In addition to that, the profitability of storage is limited through a certain loss of dry matter caused by respiration.

Both the kernels respiration and the respiration of microorganisms which are living on the kernels, contribute to the total amount of respiration. Some authors (Dierchen 1953; Gilman and Barron 1930;

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Hummel *et al.* 1954; Milner *et al.* 1947) say the microorganisms portion of the total amount of respiration is larger than the portion of the enzymic conversions within the kernel. To examine how much the microorganisms living on the kernels surface contribute to the total amount of respiration, preliminary investigations were carried out. For these investigations the kernels were sterilized on the surface by washing them using a solution of 1% sodiumhypochlorite (NaClO), as usual in microbiological experiments. The respiration activity of treated kernels was about 8% smaller than the respiration activity of untreated kernels from the same charge. This statement is valid for undamaged kernels which show no visible fungus and have been stored for less than 24 h. During the sterilization process there was no measurable change in moisture content.

The reduction of respiration rate of surface sterilized kernels leads to the conclusion that the respiration of microorganisms living on the surface of corn kernels of good quality (no visible mould) is of minor importance. The given value of about 8% is a mean value for the investigated range of moisture content (14 to 25% w.b.).

In the scope of a research project (financed by the DFG[1]) the total respiration activity of shelled corn was determined in relation to moisture content and temperature in the range of interest.

The influence of respiration activity on the efficiency of storage was ascertained with regard to quality and quantity. The quality of the stored goods is primarily influenced by the damage to the germ due to rising temperature and by deterioration due to mould growth. The results of quality measurement are not contained in this article due to space restrictions but have been reported (Scherer 1979; Scherer *et al.* 1980) already. The dry matter of the stored goods diminishes continuously due to decomposition of carbohydrates in the respiration process.

LABORATORY TESTS AND RESULTS

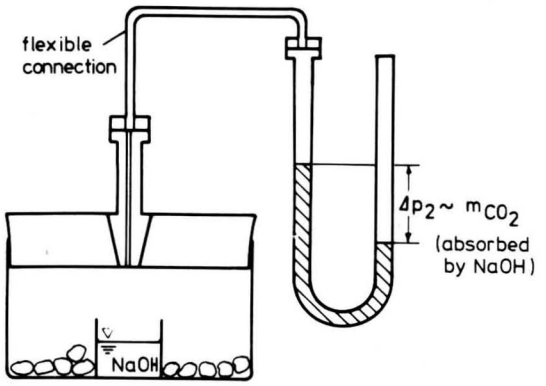
The laboratory tests to determine respiration heat and losses of dry matter have been carried out with a Warburg-apparatus (Kayser). With this the carbon dioxide (CO_2) produced by respiration is determined indirectly. The advantages of the Warburg method are: investigations can be conducted at constant and exactly defined test conditions; microscopic volumes of carbon dioxide can be detected with sufficient accuracy; the size of sample needed is about 4g to 5g (wet matter); it is comparatively fast (measuring period about 2 to 3 h after

[1] Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg

temperature equilibrium) and last but not least, it is possible to do up to ten parallel tests with different materials with one apparatus and at the same time.

Figure 1 shows the principle of the testing equipment used. In the vitreous reaction vessel are about 4g corn and 0.5 ml sodium hydroxide (NaOH) solution of 25%. The reaction vessel is linked to a manometer with twin capillaries by a flexible steel connection. The manometer is filled with a special liquid (Brodie's solution; $\rho = 1033\ kg/m^3$). The reaction vessels are moved within a constant tempered ($\delta\theta \leqq \pm 0.05$ K) water basin to make sure all carbon dioxide contained in the reaction vessel will be absorbed by the sodium hydroxide due to the air circulation caused by moving the vessels. From the manometer one can read a negative pressure, which is proportional to the absorbed volume of carbon dioxide, correction for barometric changes provided.

With this equipment, tests have been carried out with different varieties of corn for several years. It was apparent that there is neither a significant influence by the variety nor a significant influence by the year of harvest on respiration activity. Rather the differences dependent on different growing areas, time of harvest and kernel size often were greater than those between individual varieties or individual years of harvest, respectively. These statements refer to undamaged corn kernels within the investigated range of moisture content between 10% and 40% wet basis (w.b.) and to temperatures from 5°C and 50°C.



$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + 2822\,kJ/mol$$

$$1\,mg\ CO_2 \triangleq 0{,}648\ mg\ TS$$

$$1\,mg\ CO_2 \triangleq 10{,}68\ 10^{-3}\,kJ$$

FIG. 1. SCHEMATIC OF THE WARBURG-APPARATUS USED TO DETERMINE THE RESPIRATION HEAT

DISCUSSION

The total heat of respiration rises progressively with increasing moisture content within the investigated range of moisture content, (Fig. 2). Decisive for that is the rapidly increasing enzyme activity, which is above all promoted by the fact that, as former investigations showed, above a moisture content of about 22% (w.b.) not all the water contained in a kernel is bound (Mühlbauer and Scherer 1977). Regression analysis verified that the dependence of respiration heat $\dot{Q}$ on moisture content M_W, as is to be expected in biological processes of that kind, may be expressed as an exponential equation of the form:

$$\dot{Q} = a \cdot e^{b \cdot M_W} \tag{1}$$

For that reason the measured points for each temperature should be exactly on a straight line in the semilogarithmic plot in Fig. 2. The points, which represent means of 3 to 7 measurements, are in good

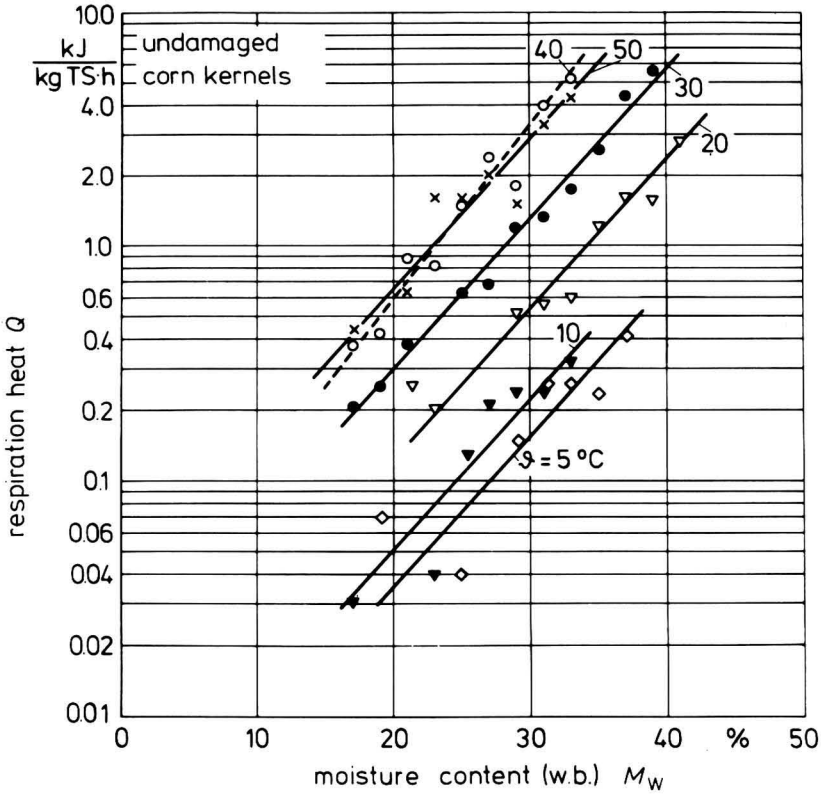


FIG. 2. HEAT OF RESPIRATION AT DIFFERENT TEMPERATURES VERSUS MOISTURE CONTENT (W.B.)

accordance with these lines. Coefficients a and b in Eq. (1) are dependent upon temperature and were evaluated separately for each temperature investigated.

The values of respiration heat below 30°C increase progressively with temperature in the form of an exponential function, (Fig. 3). Starting at about 30°C to 35°C the rise steadily decreases (the graph flattens out) up to about 45°C to above 50°C, where the maximum of the respiration activity is reached. Both the limit up to which the values of respiraton activity grow like an exponential function and the point where the maximum is, depend upon the moisture content of the grain and are located at higher temperatures the drier the grains are.

The development of a maximum of respiration activity and the decrease at further increasing temperature can be explained by the destruction of the enzymes being responsible for the chemical conversions in the respiration process. This speculation is verified by comparing the values shown above with those, which were determined using

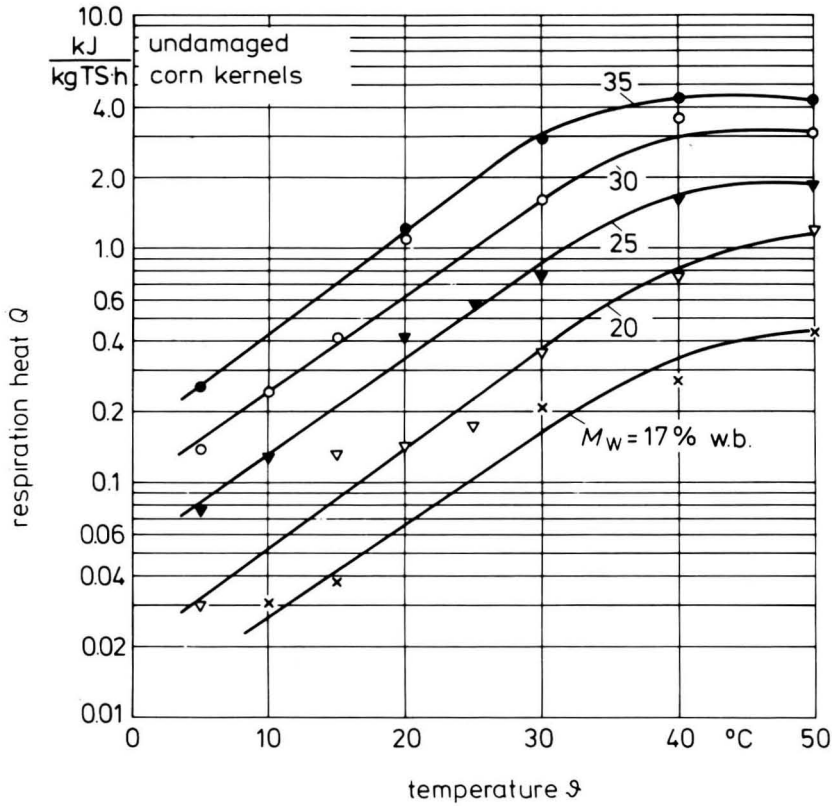


FIG. 3. RESPIRATION HEAT DEPENDENT UPON TEMPERATURE AT DIFFERENT MOISTURE CONTENTS (W.B.)

corn, predried at high temperatures. During the high temperature ($\theta > 60°$ C) predrying process a part of the enzymes were destroyed, therefore the kernels respire less than naturally dried corn at the same moisture content.

Due to the flattening out of the graphs from 30°C to 35°C the respiration heat dependent upon temperature can be reproduced below that temperature range by

$$\dot{Q} = c \cdot e^{d \cdot M_W} \tag{2}$$

with good accuracy.

Equation (2) may be used to calculate the respiration heat with sufficient accuracy up to temperatures of about 40°C for corn of less than 25% moisture content (w.b.). The coefficients c and d depend upon the moisture content of the grain and have to be evaluated separately for each (small) range of moisture content.

With Eq. (1) and (2), respectively, one can calculate the quantity of heat produced during the respiration process with very good approximation to the measured data. For high demands on accuracy of these calculations, nevertheless, it is necessary to determine the coefficients a and b or c and d in advance, because these coefficients are only true for a specific, constant temperature or a specific, constant moisture content, respectively. To avoid this disadvantage, a multiple linear regression analysis was carried out after logarithmic transformation of the measured data. All data of a few years which lie in the temperature and moisture ranges described below were taken into account.

The aim of this regression analysis was to be able to give *one* equation with constant coefficients to calculate the respiration heat, which is applicable to the most extensive range of moisture content and temperature possible without having to sacrifice accuracy.

The equation

$$\dot{Q} = 0.963\, e^{(0.092\theta + 0.152 M_W)} \qquad r = 0.981 \tag{3}$$

$\dot{Q}$	kJ/kg $TS \cdot h$	respiration heat
θ	° C	temperature (5° C $\leqq \theta \leqq$ 40° C)
M_W	%	moisture content of kernels (w.b.) (10% $\leqq M_W \leqq$ 35%)
r	–	correlation coefficient

represents the result of the regression analysis. The correlation coefficient r, which is almost 1, substantiates the admissibility of this action and verifies the kind of equation chosen. Solely for moisture contents over 30% (w.b.) the calculation of respiration heat with Eq. (3) supplies

too high values because respiration activity has it's maximum for high moisture contents already at about 40°C. If one takes this restriction into account, with Eq. (3) a useful instrument for optimal design of (aeration) bins considering respiration is now available.

FIELD TESTS AND RESULTS

A precondition for the utilization of Eq. (3) for designing (aeration) bins is still the proof that the data measured in the laboratory corresponds with that under the conditions occuring in full scale bins. Therefore, simultaneous tests under conditions similar to those in practical operation were carried out with corn harvested under the same conditions. With aerated bins the difference of carbon dioxide (CO_2) content of the air before and after flowing through the bin was measured using an infrared absorption spectrometer (URAS). From this difference of carbon dioxide concentration the respiration heat produced can be infered.

In Fig. 4 a schematic of the test equipment is shown. The 2 m high by 0.6 m diameter bins were well insulated to simulate conditions similar to those in practice. Equidistantly (0.2 m) airtight apertures were installed to ascertain temperature and moisture content of the kernels in the bin dependent on location. The air was forced through a special cooler to achieve greater measurement accuracy with the analyser.

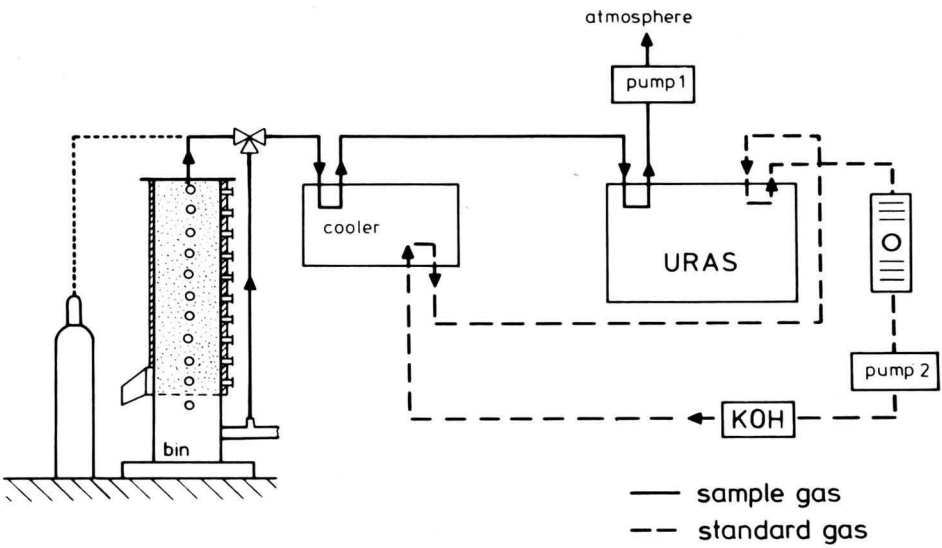


FIG. 4. SCHEMATIC OF THE TEST EQUIPMENT USED TO DETERMINE RESPIRATION HEAT AND LOSSES OF DRY MATTER DURING IN BIN DRYING.

From the difference of carbon dioxide concentration between fresh air and exhaust (δ CO_2), air flow rate $\dot{V}_L$ and mass of dry matter m_{TS} of the aerated goods, the respiration heat produced per time unit can be calculated with the following equation:

$$\dot{Q} = k \frac{\delta\ CO_2 \cdot \dot{V}_l}{m_{TS}} \tag{4}$$

The constant k contains the conversion factors needed to evaluate respiration heat in kJ from the difference in carbon dioxide concentration in ppm. It takes care of density changes due to temperature differences between the bins and the measuring chamber of the URAS and also considers the law of Gay-Lussac and the oxidation equation given in Fig. 1.

The respiration heat production evaluated using Eq. (4) versus the time the corn stays in the bins is shown in Fig. 5 for two different test conditions. The diagrams on the left hand side are valid for naturally moist corn which has been cleaned and stored immediately after harvesting. To illustrate the influence of predrying at high temperatures, the same facts are shown for corn, predried at high temperatures to 24.3% moisture content (w.b.), on the right hand side. To predry the corn a combined concurrent-flow (θ = 200° C; v_L = 1.0 m/s) /counter-flow (θ = 120° C; v_L = 0.5 m/s) dryer was used.

DISCUSSION

For both cases shown in Fig. 5 one can see that it is no longer possible to record the quantity of respiration activity with the test equipment used from that point onwards at which the corn in all layers reached a moisture content of about 20% (w.b.) or less. It is also obvious that due to the high temperature of predrying, the respiration rate at the same moisture content is smaller than it is for untreated corn. The decrease of respiration activity of predried corn is steeper than it is for untreated corn due to the sterilization effect of the high temperatures and due to the partial destruction of the enzymes responsible for the chemical conversions.

Comparison With Previously Published Data

Table 1 gives an almost complete comparison of respiration data available for corn. The obviously large differences between the values determined by different authors may have occured due to four main reasons: (1) differences in sample preparation, for example: predrying, rewetting; storage time before carrying out the tests, etc. (2) different

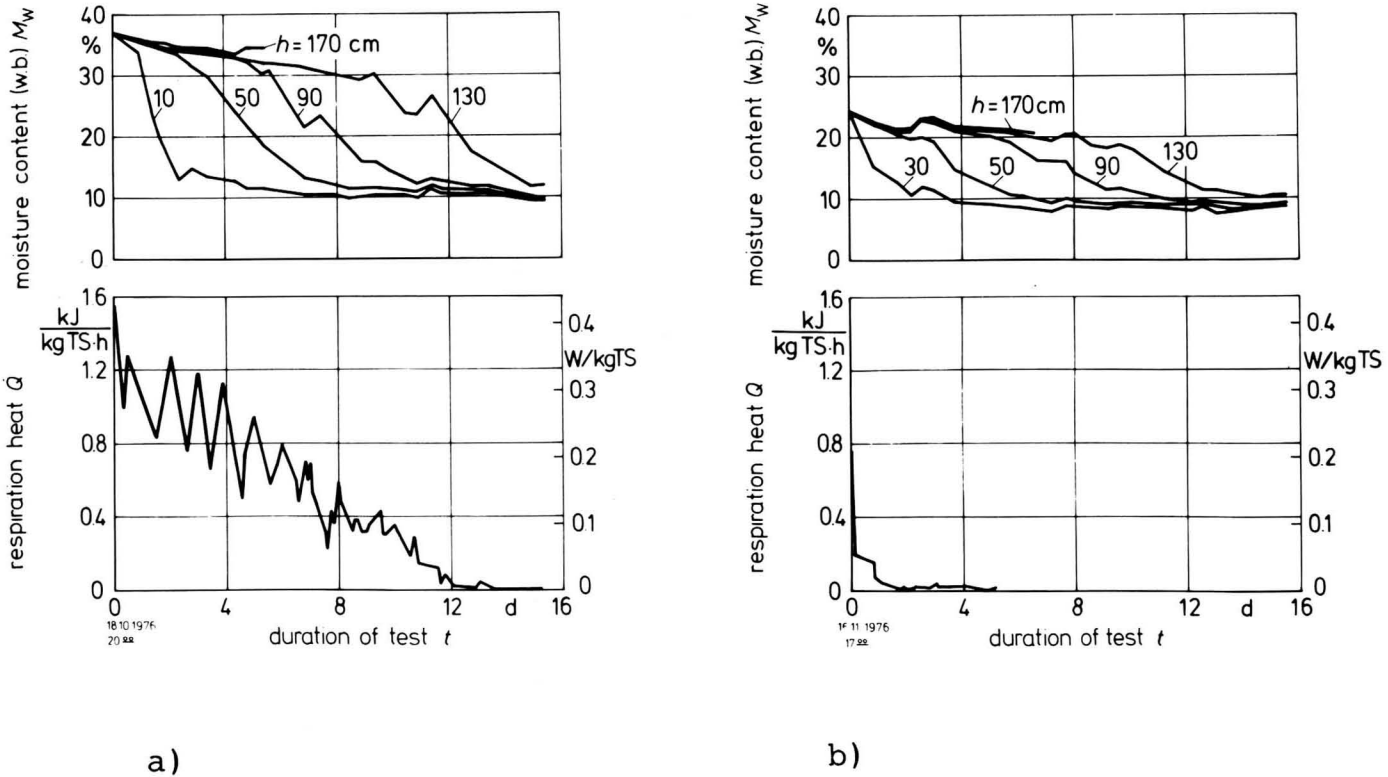


FIG. 5. RESPIRATION HEAT AND MOISTURE CONTENT DEPENDENT UPON DURATION OF TEST FOR:

a) Naturally moist (M_W = 35.9 % w.b.) and
b) Predried corn (M_W = 24.3 % w.b.)

Table 1. Respiration heat, literature summary

Author	Method	Sample Preparation	Moisture Content % w.b.	Test Conditions	Respiration Heat J/kgTS· h
Bailey, C.H.	Aerated chambers, titration of the output air	Rewetted	11.0–17.0	ϑ = 37.8 C°	3.0–100
Olafson, J.H. *et al.*	Aerated at controlled rates, CO_2 measurement with a spirometer	Rewetted	12.9–19.0	ϑ = 30 C° Grade No 1–5 t = 10–14 days	0.1–703.7
Saul and Lind	Heinicke-gas-train-method, aerated	Natural moist artificially predried	19.0–28.0	$\vartheta \sim$ 20 C° t = 0–48 days	0.1–341.2
Steele, Saul and Hukill	Aerated with CO_2 free air, CO_2-measurement in the output air by absorption at Ascarite	Handshelled -comb. harvested	13–32	ϑ = 1.5–49 C° t = 0–300 h different damaged	0.1–1030.3
Zimmer, E. *et al.*	1) CO_2-concentration in exhaust air 2) not described	Natural moist	40.0	ϑ uncontrolled 1) aerated bins 2) airtight bottles	whole kernels / shredded kernels 1) 254.5 / 393.4 2) 295.0 / 519.6
this paper	Manometric method, CO_2-free atmosphere	Moisture content at harvest 40%; dried by aeration	10.5–34.0 13.7–42.0 16.0–42.0 6.0–40.0	ϑ = 10 C° ϑ = 20 C° ϑ = 30 C° ϑ = 40 C°	5.7– 323.9 13.7–2800.0 209.1–5607.0 49.5–2457.9

methods of determination: Warburg-method; Heinicke-gas-train-method; titration; gas concentration ... which conducts to various boundary conditions in terms of O_2 and CO_2 content of the surrounding atmosphere. (3) Duration of test. Zimmer *et al.* (1973) showed, that at least from the 10th day on respiration rate decreases; and (4) Sample composition: size and shape of kernels; foreign material (cob or leave parts); degree of damage; microorganism population, etc.

CONCLUSION

To determine respiration activity, laboratory (using a Warburg-apparatus) and field (with aerated bins) tests were carried out. The investigated range of moisture content was about 10 to 40% w.b. at temperatures between 5 and 50°C.

Respiration heat production in aeration was calculated on the basis of data obtained in laboratory tests to check the agreement with the results of the field tests. Due to the moisture and temperature gradient in the bulk heat production at the present conditions had to be calculated step by step for each layer. This was done by integration of the values determined in laboratory tests under the conditions (moisture content, temperature) in the bulk.

Total heat production in the bin is the sum of the calculated values for the several layers.

In both cases, with naturally moist corn and with high temperature predried corn, the agreement between calculated and measured values was good. The differences were less than the added errors of measurement of the Warburg-apparatus (± 3.5%) and the ultra-red-absorption-spectrometer (± 3.3%) (Scherer 1979).

The Eq. (3), developed here allows calculation of the heat production and the dry matter losses caused by respiration. Extensive investigations to determine respiration activity dependent upon moisture content and temperature were carried out. Representative results of these investigations are shown in Fig. 2, 3 and 5.

LIST OF SYMBOLS

a,b,c,d,k	-	constants
m_{TS}	kg	dry substance (index *TS* means dry matter)
$\dot{Q}$	kJ/kg $TS \cdot h$	respiration heat (kg *TS* = kg dry matter)
r	-	coefficient of correlation
M_W	%	moisture content (wet basis)

v_L	m/s	air velocity
$\dot{V}_L$	m^3/s	air-volume flow rate
θ	°C	temperature
ρ	kg/m^3	density

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USE OF THE BIRD-LEIDER EQUATION IN FOOD RHEOLOGY

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ABSTRACT

Shear stress development at inception of a constant shear rate was studied for marshmallow cream, peanut butter, squeeze margarine, tub margarine, whipped butter, whipped cream cheese and whipped dessert topping using the cone and plate geometry of the Rheometrics Mechanical Spectrometer. For most foods studied transient shear stresses showed increasing shear stress oversoots with increasing shear rate. At the highest shear rate of 100 s^{-1}, transient stresses were as large as 425% of the steady state shear stresses, with the actual magnitude of overshoot depending on the particular food investigated.

The Bird-Leider equation was chosen to model this time dependent flow behavior by incorporating both steady viscous and elastic properties of the foods. By assuming that the viscosity function and primary normal stress coefficient followed power-law behavior, and constructing a time constant from the calculated parameters, the Bird-Leider model provided a good prediction of maximum and steady state stresses as well as the time at which they occur, but only a crude prediction of shear stress decay. The model supplied two more empirical constants "a" and "b" where "a" can be regarded as a pseudo-elastic modulus. Variation in "a" with shear rate shows that all materials studied are nonlinear viscoelastic.

INTRODUCTION

Fluid and semisolid food materials exhibit shear flow behavior which is both strain and rate of strain dependent. This introduces a time dependent behavior in simple shear flow since the total strain the material undergoes is a functon of time. These materials are viscoelastic, and the elastic component generates transient perturbations in

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shear stresses which must be taken into account for proper design of flow equipment such as pumps, extruders, mixers etc., for accurate prediction of texture.

Rheological equations which relate shear stress, shear rate strain and time in order to predict transient viscoelastic flow behavior have been developed to explain viscoelastic flow behavior in polymeric materials (Bird *et al.* 1977) Such models include the Bogue-Chen model, the Carreau model, the Spriggs model and the Bird-Leider model. A review of these models is given by Leppard and Christiansen (1975). However, these models have not been tested with food materials. Preliminary data has been obtained by DeMann (1969) for margarine, and by Elliott and Ganz (1971) using mayonnaise, whipped and unwhipped margarine.

In the present study, an attempt is made to characterize shear stress development in commercial peanut butter, marshmallow cream, squeeze margarine, tub margarine, whipped butter, whipped cream cheese and whipped dessert topping using the Bird-Leider model. The Bird-Leider model is an empirical viscoelastic flow model where material properties are obtained by curve fitting steady and transient shear stress and steady normal stress data (Leider and Bird 1974). This equation has the following form:

$$\tau_{\theta\phi} = m(\dot{\gamma})^n[1 + (b\dot{\gamma}t - 1)\exp(-t/an\lambda)] \quad (1)$$

where $\tau_{\theta\phi}$: shear stress
m,n: limiting viscous power-law parameters
γ: shear rate
t: time
a,b: adjustable parameters
λ: time constant.

where

$$\lambda = \left(\frac{m'}{2m}\right)^{1/n'-n}$$

m', n';
first normal stress power-law parameters

A distinct convenience of this equation is that at long times, it converges to the power-law, a steady flow behavior observed with many food materials (Rha 1978; Rao 1977).

EXPERIMENTAL

The rheological measurements were carried out at room temperature (24°C to 27°C) using the cone and plate geometry of the Rheometrics Mechanical Spectrometer. In all cases, the cone radius was 1.25 cm with a cone angle of 0.04 radians. A 0-100 gm-cm transducer was used for all foods except peanut butter, which required a 0-2000 gm-cm transducer.

To eliminate the effect of shear history, a new sample was used for each measurement. It must, however, be noted that sample pretreatment can be critical in determining the magnitude of the material transient response (Bagley and Taylor 1974). Measurements were repeated five times at each shear rate. Stress growth measurements were carried out at shear rates of .1, 1, 10 and 100 s^{-1}. In addition to the four shear rates studied, shear stress growth data was obtained at three other shear rates in order to fully characterize the steady rheology of each food. Due to a transducer overload, no data is reported for marshmallow cream at a shear rate of 100.0 s^{-1}. Other control problems encountered when collecting data are discussed elsewhere (Kokini and Dickie 1981). It must, however, be emphasized here that apparent stress transients, particularly that of normal stress have been reported to depend on the geometry of the apparatus, specifically on cone angle and cone diameter. (Crawley and Graessley 1977) Meissner (1972) has found such effects to be associated with the torsional and axial stiffners of the instrument. This particular study did not in any way specifically concentrate on instrument and geometry effects. Typical variation in shear stress growth data and normal stress growth data are illustrated in Fig. 3 and 4.

RESULTS

When steady shear stress versus shear rate data was analyzed, it was found that apparent viscosities followed power-law behavior (Fig. 1). For the foods studied, the smallest n value was 0.057 for whipped butter and the largest n value was 0.379 for marshmallow cream. The m values ranged from 8.68 Pa s^n for squeeze margarine to 563.10 Pa s^n for marshmallow cream. All values for m and n are listed in Table 1. Comparison of steady data for peanut butter with that previously obtained by Shama and Sherman (1973) shows that the agreement is good. Primary normal stress coefficients also followed power-law behavior as indicated by the straight line obtained when plotting the primary normal stress coefficient versus shear rate on log-log coordinates (Fig. 2). The slope of each line in Fig. 2 is equal to $n' - 2$ and m'

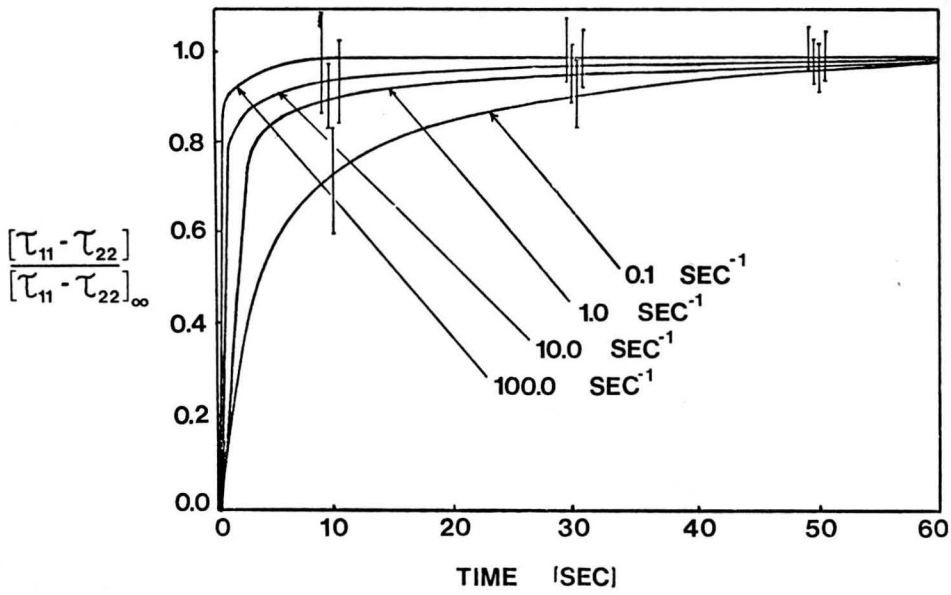

FIG. 1. NORMAL STRESS DEVELOPMENT [PEANUT BUTTER AT 25°C]

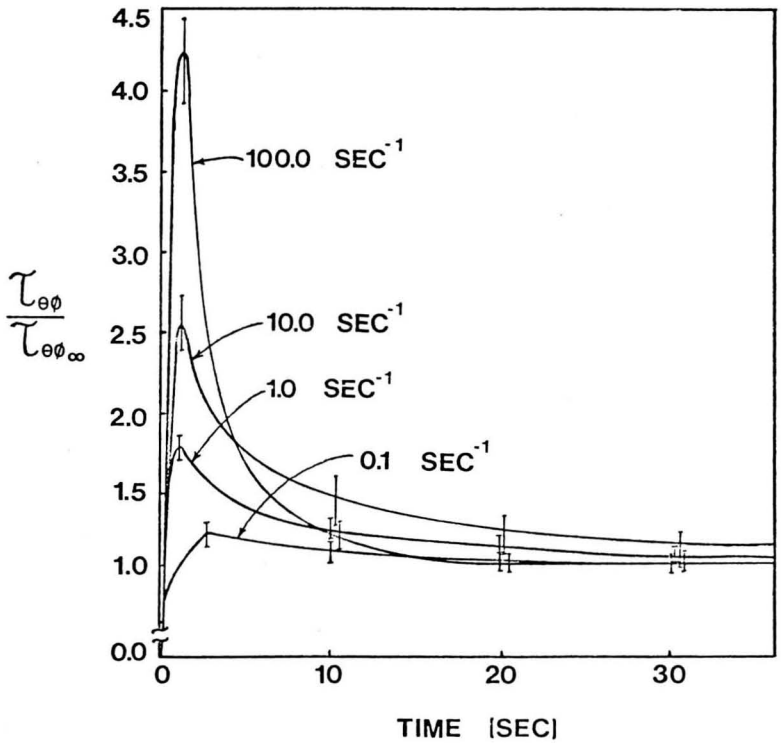

FIG. 2. SHEAR STRESS DEVELOPMENT [PEANUT BUTTER AT 25°C]

Table 1. Viscoelastic parameters of foods

	m (Pa s^n)	n	R^2	m' (Pa $s^{n'}$)	n'	R^2	λ (s)
Whipped butter	$3.1 \pm .4 \times 10^2$	.057	.99	$1.1 \pm .1 \times 10^2$	.476	.99	1.61×10^{-2}
Whipped cream cheese	$4.2 \pm .5 \times 10^2$	.058	.99	$3.6 \pm .2 \times 10^2$	.418	.99	8.60×10^{-2}
Squeeze margarine	$8.7 \pm .8 \times 10^0$	.124	.99	$1.6 \pm .4 \times 10^1$	.168	.99	9.93×10^{-2}
Tub margarine	$1.1 \pm .1 \times 10^2$	.077	.99	$1.8 \pm .3 \times 10^2$	.358	.99	5.16×10^{-1}
Whipped dessert topping	$3.6 \pm 1. \times 10^1$	.120	.99	$1.4 \pm .5 \times 10^2$	.309	.99	3.09×10^1
Marshmallow cream	$5.6 \pm .2 \times 10^2$	.379	.99	$1.9 \pm .3 \times 10^2$	.127	.99	1.27×10^3
Peanut butter	$5.0 \pm .7 \times 10^2$	.065	.99	$3.8 \pm .1 \times 10^3$	.175	.99	1.86×10^5

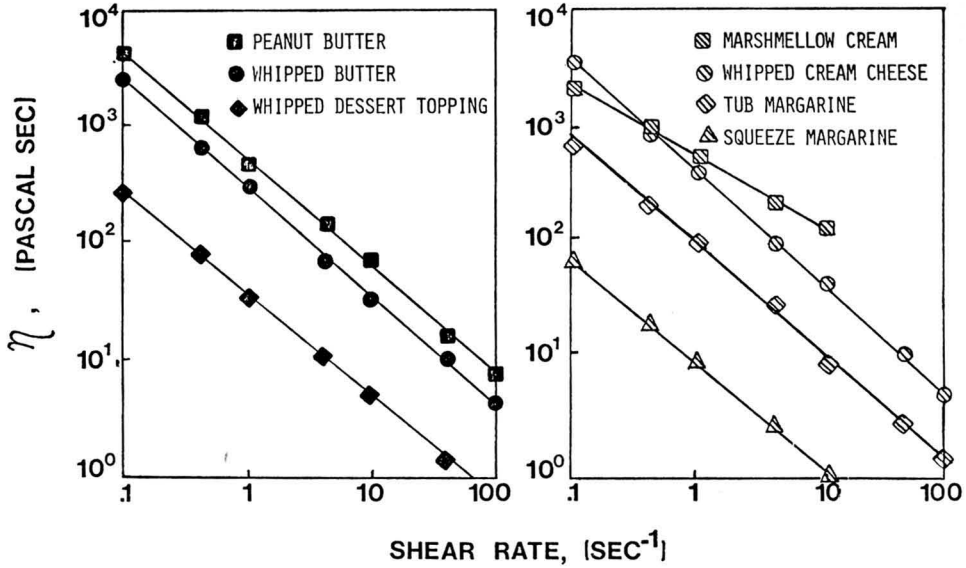

FIG. 3. VISCOSITY VERSUS SHEAR RATE

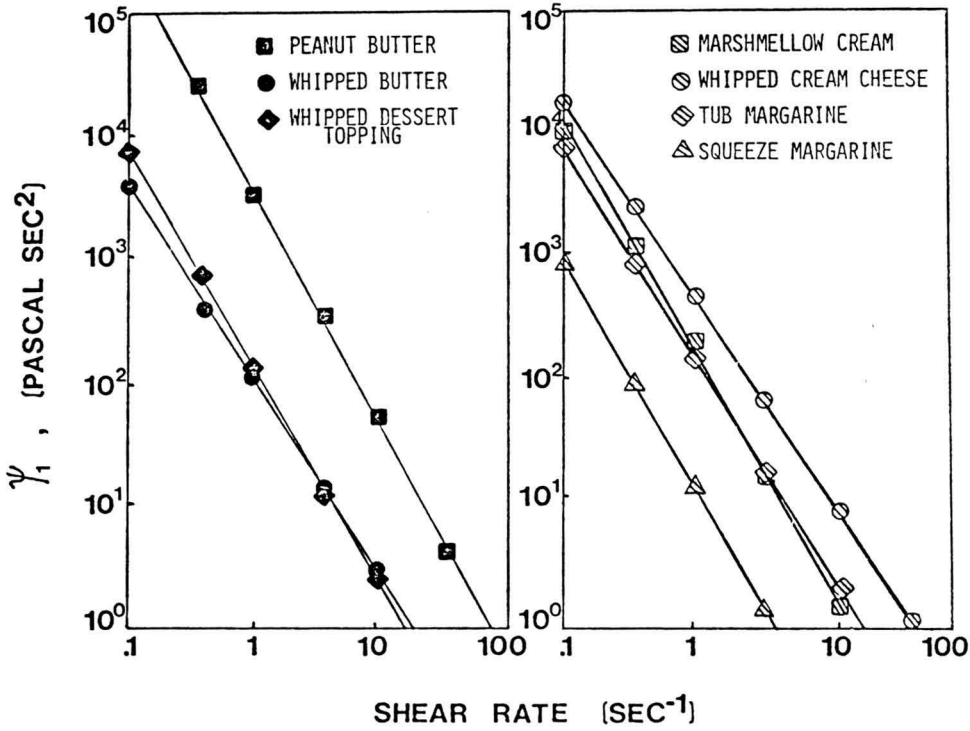

FIG. 4. PRIMARY NORMAL STRESS COEFFICIENT VERSUS SHEAR RATE

values are found at a shear rate of 1.0 s^{-1}. The values of n' ranged from 0.127 to 0.476 for marshmallow cream and whipped butter respectively; m' values ranged from 15.70 Pa $s^{n'}$ for squeeze margarine to 3785.00 Pa $s^{n'}$ for peanut butter. It is of interest to note that the relative magnitude of m tended to follow relative magnitudes of m'.

Values for λ calculated from m, m', n and n' ranged from 1.61×10^{-2} to 1.86×10^{5} s. The thickest foods such as marshmallow cream and peanut butter displayed large time constants. Squeeze margarine, the most fluid food studied, displayed a time constant of 9.93×10^{-2} s; quite small compared to peanut butter.

An example of normal stress development data is shown in Fig. 1 for peanut butter at 25°C. It is interesting to note that normal stresses did not overshoot. They also tended to grow to their steady state value fastest at the higher shear rates. This is in contrast to most polymeric materials which tend to show normal stress overshoots next to shear stress overshoots. However, this result seems to be consistent with the Doi-Edwards Theory. (Doi and Edwards 1979)

Shear Stress growth data for all foods is presented in Fig. 5 to 11. The transient data is presented as the ratio of shear stress at any given time to steady state shear stress. In Fig. 5 for marshmallow cream

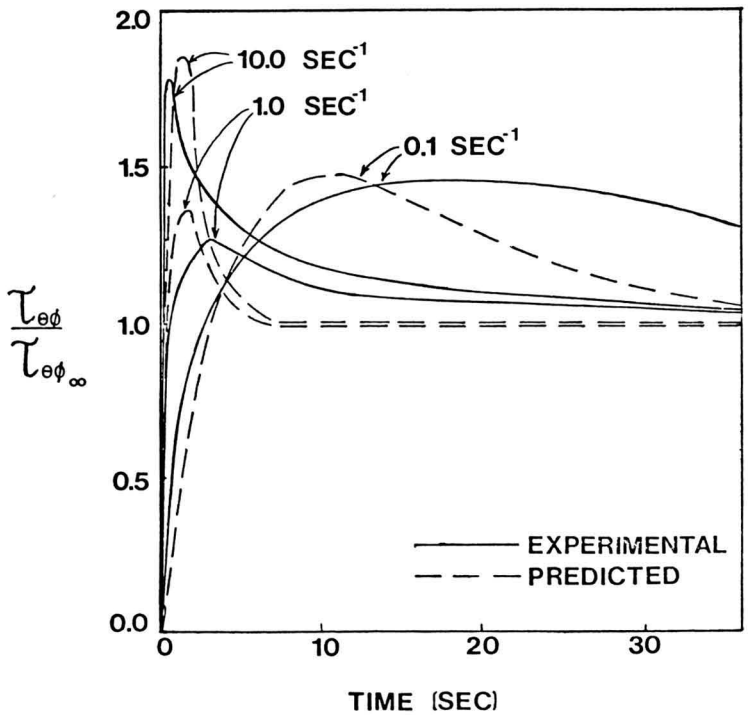

FIG. 5. SHEAR STRESS DEVELOPMENT [MARSHMALLOW CREAM AT 25°C]

stress overshoot at a shear rate of .1 s^{-1} reaches 1.4 times the steady shear stress value. The magnitude of overshoot at 1.0 s^{-1} was less than that at the smaller shear rate of 0.1 s^{-1}, being only 25% of the steady shear stress. This behavior seems to be an exception to the general observation that the magnitude of stress overshoot increases with increasing shear rate. At a shear rate of 10.0 s^{-1}, the peak stress value was 75% greater than the steady stress value. Although the magnitude of overshoot did not increase with increasing shear rate for the three shear rates, the time at which the peak occurred was smallest at the greatest shear rate and decreased with increasing shear rate. This phenomena is consistent with experiments using polymeric materials (Lee and Brodkey 1971; and Huppler *et al.* 1967).

For peanut butter in Fig. 6, overshoots were quite substantial at all shear rates and stresses decayed to a steady state rapidly. Peak stresses ranged from 25% to over 400% of the steady state value with the extent of oversoot increasing as shear rate increased. Times of peak stresses ranged from 0.5 s to 3.0 s with the actual time decreasing with increasing shear rate.

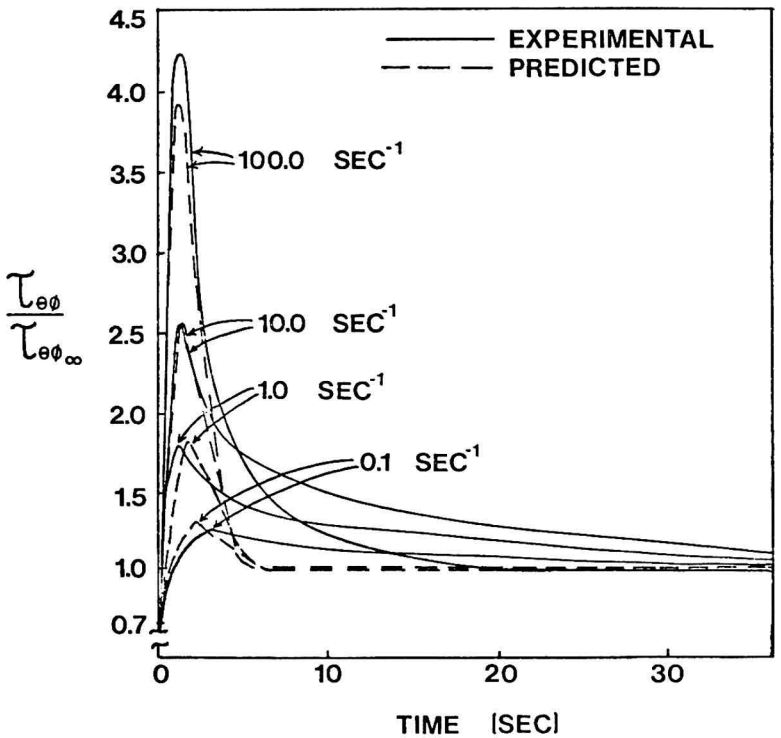

FIG. 6. SHEAR STRESS DEVELOPMENT [PEANUT BUTTER AT 25°C]

For squeeze margarine at shear rates of 0.1, 1.0, and 10.0 s^{-1}, the peak overshoot was approximately 25% greater that the steady state shear stress (Fig. 7). Exponential decay to the steady state shear stress value was relatively slow at all three shear rates. Although the magnitude of overshoot did not increase significantly, the time the peaks were reached did decrease as shear rate increased. The peak overshoot at 100.0 s^{-1} was 100% greater than the equilibrium stress with decay occuring slowly. The time at which the maximum shear stress occurred was again smallest at the shear rate of 100.0 s^{-1}.

For tub margarine in Fig. 8, overshoots at 0.01 and 1.0 s^{-1} are small compared to overshoots at 10.0 and 100.0 s^{-1}. Peak overshoots occurred within two seconds with a slow decrease in stress until steady state was reached. Relaxation time to the steady stress was largest at 10.0 s^{-1}. There was only a gradual decrease to a steady state. At 100.0 s^{-1}, the maximum overshoot value occurred at 0.5 s, at which time a rapid decrease in shear stress was seen. At approximately 5 s, transient stress

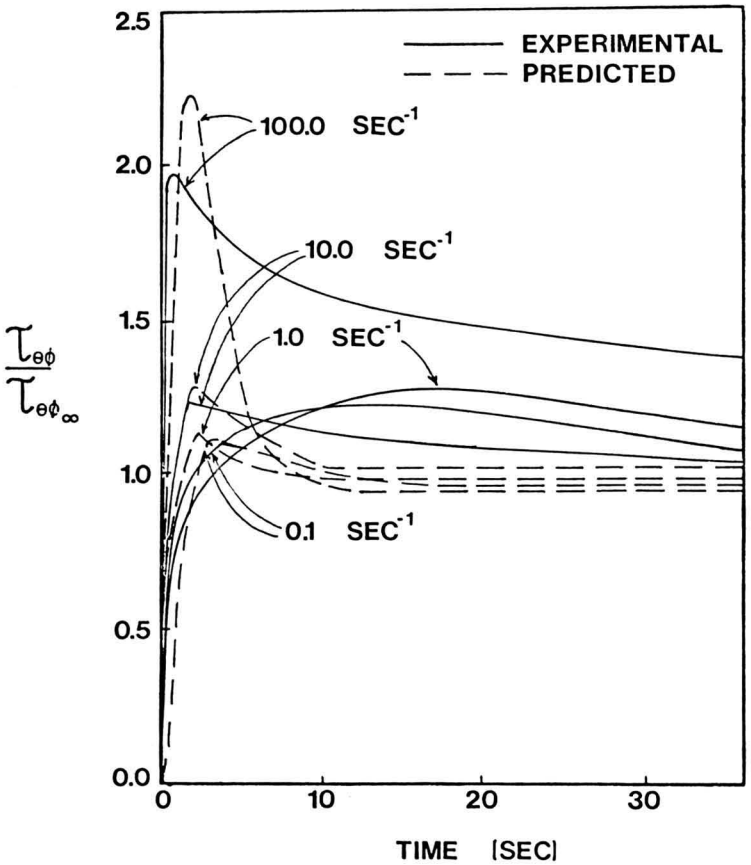

FIG. 7. SHEAR STRESS DEVELOPMENT [SQUEEZE MARGARINE AT 25°C]

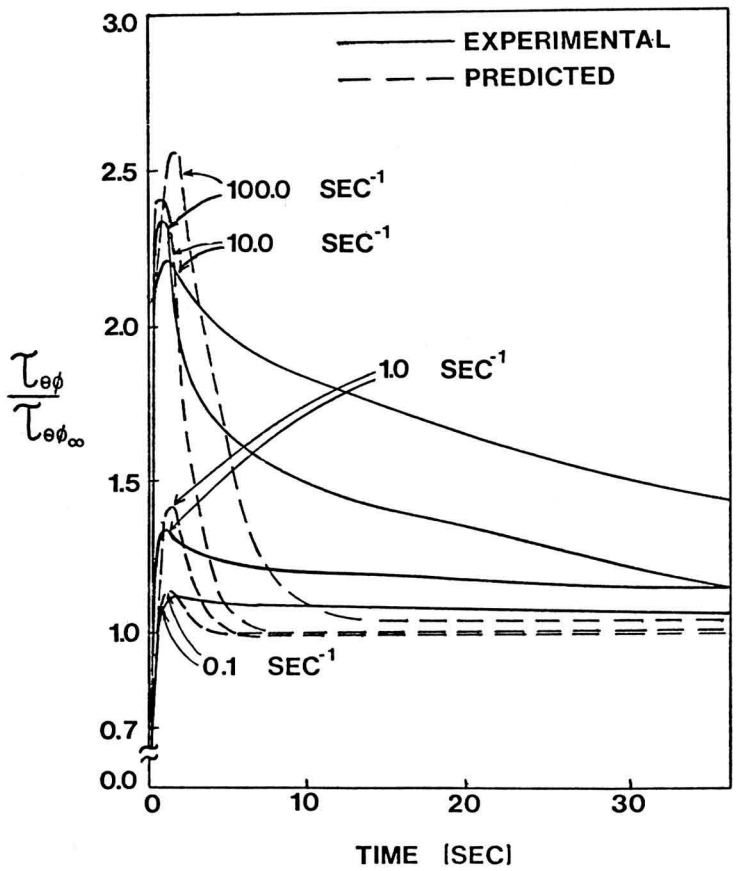

FIG. 8. SHEAR STRESS DEVELOPMENT [TUB MARGARINE AT 25°C]

decayed less rapidly, paralleling the decay observed at 10.0 s^{-1}.

Figure 9 shows shear stress development versus time data for whipped butter. At 0.1 s^{-1}, shear stress grew with little overshoot (10%) while at larger shear rates, peak overshoots were larger (50% to 100% greater that equilibrium values). In all cases, peak stresses were reached rapidly, within 3 s of inception of steady shearing. At 1.0 s^{-1}, after the peak stress was reached, stresses relaxed to a steady state within 15 s. The decay in stress at 10.0 s^{-1} and 100.0 s^{-1} was slower.

Again, in Fig. 10 for whipped cream cheese, we see the same phenomenon as in marshmallow cream. At a shear rate of 10.0 s^{-1}, the peak overshoot value is larger than at 100.0 s^{-1}. At both shear rates, peak values occur at 0.5 s, at which time stresses decayed quickly for 5 s and then the rate of decay decreased allowing for a long relaxation time until steady state is reached. At 0.1 and 1.0 s^{-1}, overshoots were relatively small and decay in stress was gradual.

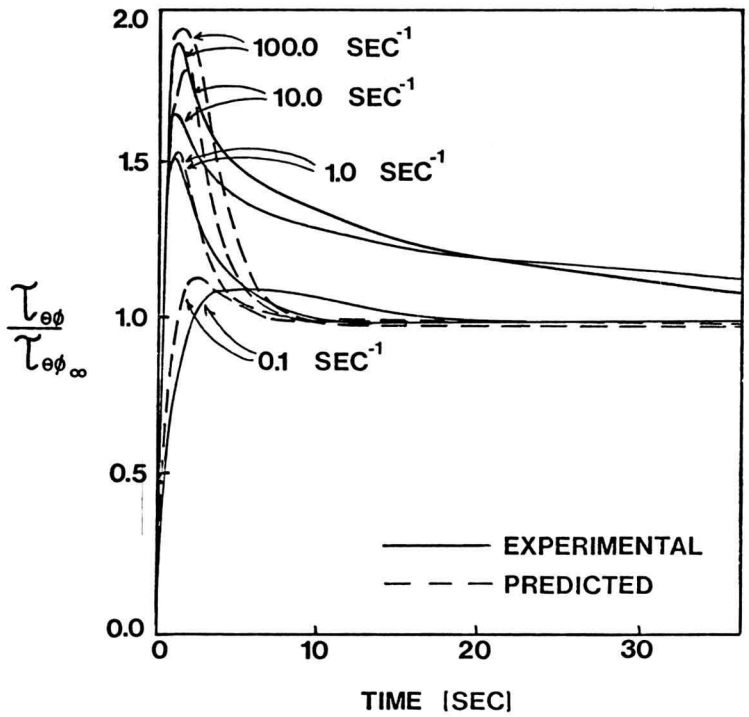

FIG. 9. SHEAR STRESS DEVELOPMENT [WHIPPED BUTTER AT 25°C]

In Fig. 11 for whipped dessert topping, overshoot increased with increasing shear rate. Magnitudes ranged from approximately 10% to 100% of the steady state shear stress values. Equilibrium was reached within 60 s at all shea rates. Peak values in stress occurred within 2 s of inception of steady shear and decayed rapidly at all four shear rates.

To predict transient shear stresses using the Bird-Leider Equation, in addition to the steady power-law parameters m, n, m', and n' and the time constant λ, the values of a and b were estimated using a Statistical Analysis System, nonlinear least squares curve fitting procedure. Table 2 lists the best values for the two constants. The overall R^2 of experimental data versus calculated values using the model for all foods at all shear rates investigated was 0.98. In Fig. 5 to 11, the predicted transient shear stresses are represented as dashed lines.

In fig. 5 for marshmallow cream, at all shear rates, peak shear stresses are well predicted and occur within 0.5 to 1 s of the actual overshoot peak. The model slightly overpredicts the experimental data. The predicted exponential decay to a steady state shear stress is more rapid than was observed at all shear rates.

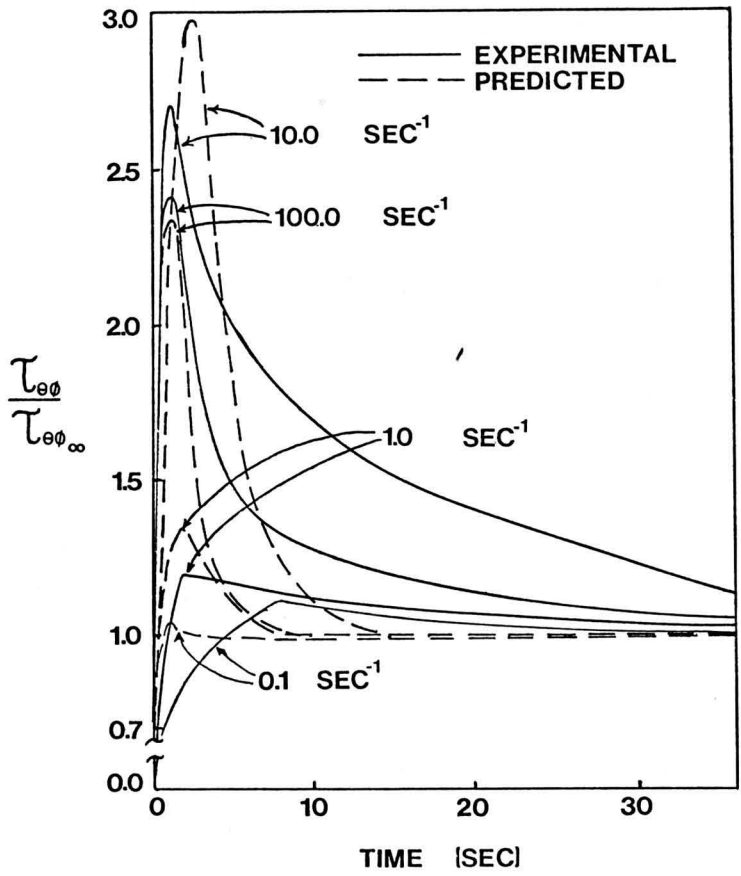

FIG. 10. SHEAR STRESS DEVELOPMENT [WHIPPED CREAM CHEESE AT 25°C]

Shear stress development is well predicted at all 4 shear rates for peanut butter (Fig. 6). Peak stresses are predicted within 10% of experimental peak values. The time at which the peaks are predicted occur within 1 s of the actual data. Although the decay portion of each curve is less well predicted than the peak or steady state region, the fit is extremely close except in the range of 5 to 10 s.

Predictions for squeeze margarine (Fig. 7) are not as good as the rest of the foods. At shear rates of 0.1 and 1.0 s^{-1}, the experimental stress reaches a maximum at 15 and 8 s respectively. Predicted times are, on the other hand, 2 s and 1.5 s, respectively. At 10.0 s^{-1}, the model does predict all portions of the shear stress development curve better, including peak, decay, steady state and the time of maximum overshoot. The preak stress is overpredicted by 15% at a shear rate of 100.0 s^{-1} and the exponential decay to steady state occurs much more slowly than the model predicts.

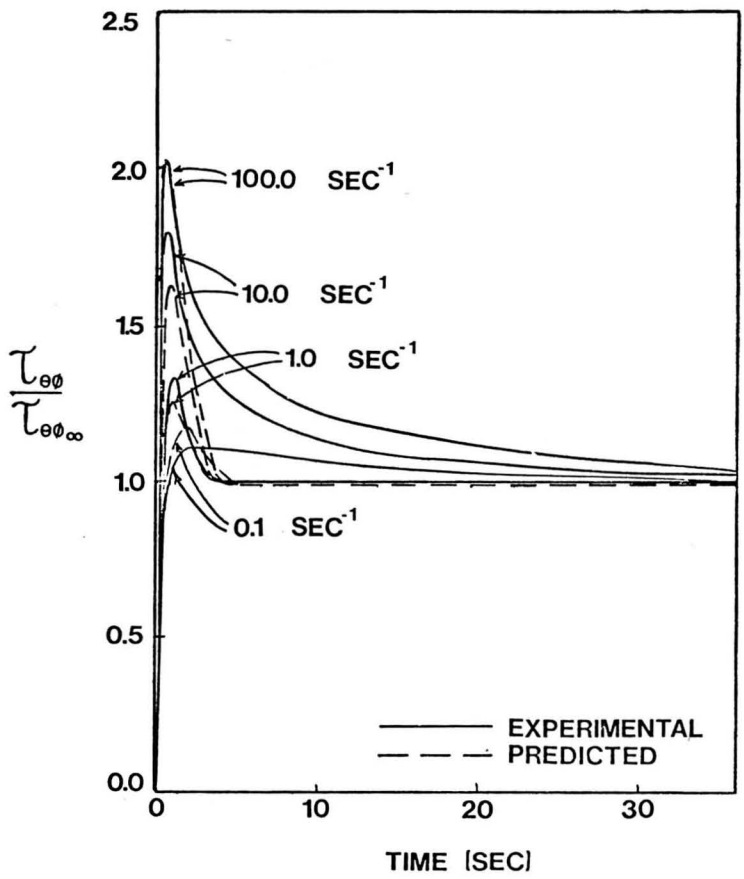

FIG. 11. SHEAR STRESS DEVELOPMENT [WHIPPED DESSERT TOPPING AT 25°C]

Peak shear stresses are moderately well predicted at all four shear rates for tub margarine in Fig. 8. Although the peak value is overpredicted in all cases, predicted peak shear stress is within 1% to 14% error. The time of maximum overshoot is also well approximated by the model, as are the steady state values for stress. However, the model does fall short in its prediction of the decay portion of the transient data. At all four shear rates, exponential decay to a steady state stress is very gradual, although the model predicts a decrease in maximum stress to steady state within 15 s of inception of steady shearing.

In Fig. 9 for whipped butter, peak stresses and times at which these peaks occurred were well predicted by the model with a maximum error of only 8%. The model did overpredict peaks slightly and again, predicted a more rapid decline in stress to a steady state value, especially at shear rates of 10.0 and 100.0 s^{-1}.

Table 2. Calculated a and b values in the Bird-Leider Equation

	$\dot{\gamma} = 0.1\ s^{-1}$			$\dot{\gamma} = 1.0\ s^{-1}$		
	b	a	R^2	b	a	R^2
Whipped butter	8.71±.99	1136.0±165.0	.99	3.13±.26	810.0±72.0	.99
Whipped cream cheese	20.0±12.0	60.1±49.0	.96	1.28±.12	257.0±23.0	.99
Squeeze margarine	5.25±1.13	156.0±46.0	.98	.94±.149	90.3±17.8	.99
Tub margarine	17.7±1.06	14.9±1.29	.99	2.48±.30	20.3±2.45	.99
Whipped dessert topping	14.0±.94	.236±.021	.99	2.70±.35	.14±.023	.99
Marshmallow cream	3.13±.48	.014±.0023	.97	1.87±.24	.0021±.00029	.99
Peanut butter	13.2±.93	.00011±.000008	.99	2.60±.16	.000099±.000007	.99
	$\dot{\gamma} = 10.0\ s^{-1}$			$\dot{\gamma} = 100.0\ s^{-1}$		
	b	a	R^2	b	a	R^2
Whipped butter	.273±.049	1258.0±165.0	.97	.034±.005	1173.0±129.0	.98
Whipped cream cheese	.377±.052	332.0±35.0	.94	.048±.007	186.0±23.0	.96
Squeeze margarine	.099±.011	81.99±15.68	.98	.037±.0046	103.0±12.0	.96
Tub margarine	.350±.035	36.50±3.59	.96	.058±.0062	20.59±2.09	.97
Whipped dessert topping	.481±.087	.142±.026	.98	.098±.0228	.103±.018	.97
Marshmallow cream	.402±.074	.0017±.00022	.98	—	—	—
Peanut butter	.554±.079	.000075±.0000097	.97	.128±.0079	.000058±.0000037	.99

Predictions for whipped cream cheese (Fig. 10) only moderately well fit the experimental data. At 0.1 s^{-1}, although the predicted peak is 8% smaller than the experimental peak, the time at which this maximum stress is predicted within 10% of experimental data with the times of peak overshoots nearly equal. The model overpredicted both the maximum stress and the time at which it occurred at a shear rate of 10.0 s^{-1}. The model predicted a more rapid decay to an equilibrium shear stress than was observed. At 100.0 s^{-1}, the model only slightly underpredicted the peak stress with only a 0.5 s difference in the time at which the peak occurred. The decay portion of the transient data was better predicted than at a shear rate of 10.0 s^{-1}, but the model still tends to allow transient stresses to decay too rapidly.

Peak and steady state shear stresses and the time at which these occur are well predicted by the model for whipped dessert topping (Fig. 11). At 0.1, 1.0 and 100.0 s^{-1}, peak overshoots are within 6% of experimental peaks with only a maximum of 0.5 s difference in time at which these peaks occur. The exponential decay portion of the data is predicted will at shear rates of 0.1 and 1.0 s^{-1}. At 100.0 s^{-1}, decay is only predicted for the first 3 s, due to the rapid decrease in the observed stress. At approximately 3 s, decay becomes less rapid and the prediction is not as good. At 10.0 s^{-1}, stresses are underpredicted by approximately 15% at all times until 15 s, at which time the predicted and experimental data begin to converge to a steady state value.

DISCUSSION

The Bird-Leider model was moderately successful in predicting transient shear stress development for the foods studied. An overall R^2 of 0.98 was obtained when comparing experimental and predicted data of all foods. The rapid increase to the maximum stress as well as the steady state shear stress data was well explained by the model. In all cases, the model underpredicted the exponential decay portion of the transient data substantially. The peak overshoot values were predicted with a 2% to 15% error.

Overshoot can be due, at least in part, to elasticity. The term $\dot{\gamma}t$ represents the total strain to which the material is subjected. It can be thought of as the initial elastic response, in which the sharp increase to the maximum stress occurs. The time at which this maximum shear stress occurs decreases as shear rate increases. This time, as well as the maximum shear stress, can easily be found by differentiating the model with respect to time at a constant shear rate and equating the derivative to zero (Kokini and Dickie 1981).

After this solid-like response to a maximum stress, the food material yields into a fluid-like state, where the exponential term in the Bird-Leider equation ($e^{-t/an\lambda}$) characterized the decay in stress until a steady shear stress is reached. At long times, the exponential term becomes zero so that the equation reduces to the power-law equation. This is particularly useful since, as shown in Fig. 1, all foods converge to power-law behavior at steady state.

The time constant λ can be thought of as a relative indicator of vicsoelastic behavior in a material. Material constants obtained from shear stress and normal stress measurements are combined to generate a property with the dimensions of time similar to the relaxation time $\lambda = \mu/G$ for a Maxwell fluid. However, although the thicker foods tended to display larger overshoots at a given shear rate while relatively fluid-like materials tended to develop small overshoots, λ is not necessarily correlated with increasing overshoot for the group of foods studied.

An interesting character of the Bird-Leider equation is its ability to demonstrate nonlinear viscoelasticity in food materials. Essentially all real materials are nonlinear when subjected to large enough strains (Darby 1976). The food materials studied are no exception to that. Parameters "a" and "b" are both shear rate dependent and clearly portray the nonlinear character. The Bird-Leider equation provides a means for predicting the time-dependent flow behavior of the foods studied, although several limitations are apparent. The Bird-Leider equation does not incorporate a yield stress term. Transient flow in foods which exhibit a significant yield stress might be better predicted if such a term was incorporated into the model. Also, because the exponential decay portion of the transient data was least well predicted, the fit of the data might be better if this term were modified using a series of relaxation terms.

CONCLUSION

The following conclusions can be drawn from this investigation. First, food materials develop considerable overshoots in shear stress which relax to a steady state shear stress value. The magnitude of this overshoot tends to increase with increasing shear rate. Second, the time at which the maximum stress occurs decreases with increasing shear rate. Thirdly, the Bird-Leider model offers a preliminary design equation for predicting the time-dependent shear stresses in the foods studied. Although the model failed to accurately describe the exponential decay in stress after the peak value was reached, it provides a good

estimate of maximum as well as steady state shear stresses. Lastly, it was shown that a long enough time, both the viscosity function and primary normal stress coefficient followed power-law behavior.

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COST OPTIMAL DEMAND FORECASTING FOR A MULTI-LABEL INVENTORY ENVIRONMENT

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ABSTRACT

A decision problem associated with the production of the same goods under several labels is anticipating how much to produce under each label. In some settings a portion of the goods is left unlabeled so that subsequent excess demand can be filled by labeling these goods held in "bright storage". This adds another decision variable to the problem and introduces some new alternatives. Attached to these alternatives facing the decision maker are several different kinds of costs depending upon the nature of the errors made in forecasting the demand for each of the labels. These costs, when associated with discrete probability distributions for the demand variables, lead to an optimization problem with nonnegative variables with objective of minimizing the decision maker's expected cost. Minor restrictions on the costs make this objective function convex. By introducing new variables the entire problem can be reformulated as a linear program. If the demand variables can take only integer values, then there is an integer, optimal solution to the bright storage problem.

INTRODUCTION

A decision problem facing manufacturers who pack the same goods under several labels is anticipating the demand for the goods and deciding how much to produce for each label. Such a circumstance occurs in the food industry when goods are packed in glass containers during a harvest period for distribution and sale throughout the remainder of the year. A traditional response to this situation has been to leave some of the goods unlabeled, so that labels may be applied later for brands for which excess demand occurs. Such storage is called "bright storage" and goods held in bright storage which are later

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labeled, cause a special per unit labeling cost to be incurred. (Leaving all the goods unlabeled until orders are received, which is sometimes done for metal containers, is not done for glass because of the high handling costs for these containers.)

Other responses and costs which may occur in the excess demand situation include unlabeling goods for a brand with excess supply and relabeling them for an excess demand case. If there is an overall shortfall when the demand for brands is considered in aggregate, an opportunity cost is incurred for not meeting demand. In the reverse situation, there is a storage and liquidation cost for goods in excess of actual demand which are still in stock at the end of the period. Each of the costs that is incurred in these situations occurs because demand is intrinsically variable. Further, each of the costs is different. The problem is to decide how much to produce under each label and how much to produce and place in bright storage. A natural criterion for choosing from the alternatives is to make this decision so that the producer minimizes expected costs.

Although the problem we investigate here has to do with a multilabel production situation, there are many analogies to other problems. In any case where the food processor faces costs because of errors in prediction, variants of these methods may be applied. A simple case would occur when the cost for a production shortfall is different than for a production overrun. The alternatives facing a processor after one or the other of these outcomes occurs are never the same, and neither are the costs. In the following, we describe a particular response to this situation, when there are several alternatives depending on the nature of the forecasting errors. These are reflected through different costs and constraints on the decision variables. Although the same function will not work in an inventory management situation, or in a quality control application, the same approach can be used to generate cost optimal forecasted information in these settings.

These problems are indirectly related to two problems previously presented in the literature. The first is L_1 approximation and the second is stochastic programming with recourse (SPR). L_1 approximation is a method of doing curve fitting which applies an alternative to the ordinary least squares curve fitting criterion commonly used in regression and time series analysis. The L_1 approximation approach requires the minimization of the sum of the absolute values instead of the sum of the squares of the deviations from the "best" curve. Because summing the absolute values results in a nondifferentiable function, minimizing this function may require a linear programming formulation of it. The connection of this problem to L_1 approximations can be seen in the later formulation of the problem as a linear program. The

deviational variables introduced are analogous to those used in the linear programming formulation of the L_1 approximation problem (Barrodale and Roberts 1970, Norback *et al.* 1979 and Wagner 1955). The connection to SPR is intrinsic to the problem. One "recourse" is the choice to label goods held in bright storage. Others include unlabeling-relabeling and liquidating excess supply. Surveys of recourse formulations and computations are found in Dempster 1980; 1968; Wets 1979 and Ziemba 1974. The perspective taken in the formulation of these problems is that when decisions are made, the decision maker expects to pay a penalty for the inaccuracy of the decision. Dempster 1980 calls the problem we face here a "Discrepancy Cost Problem" (p. 9).

PROBLEM FORMULATION

In the following $f^{(+)} = f$ if $f \geq 0$ and $f^{(+)} = 0$ otherwise. Let $Y = (Y_1, Y_2, \ldots, Y_{r-1})$ be the demand random vector for the $r-1$ labels. Let $Y_k = (Y_{k,1}, Y_{k,2}, \ldots Y_{k,(r-1)})$ be a particular realization of the demand vector and let $P_k = \text{Prob}\,(Y = Y_k)$, where the set of realizations is assumed to be finite with cardinality N and $\sum_{k=1}^{N} p_k = 1$, $p_k > 0$. Let $y = (y_1, y_2, \ldots, y_{r-1}, y_r)$ be the vector of decision variables, that is y_j is the amount to be produced and given label j, with y_r the amount to be left unlabeled in bright storage. Four distinct costs are identified:

C_1 – the cost per unit of overproducing.
C_2 – the cost per unit of labeling goods taken from bright storage.
C_3 – the cost per unit of unlabeling goods with one label and relabeling them with another.
C_4 – the cost per unit of unfilled demand.

For any realization of the demand variables, there are three cases.
The excess demand case.

$$\text{I} = \left\{y\colon y_r < \sum_{j=1}^{r-1} (Y_j - y_j)\right\}$$

where the associated cost $t = C_4\left(\sum_{j=1}^{r-1} (Y_j - y_j) - y_r\right) + C_2 y_r + C_3 \sum_{j=1}^{r-1} (y_j - Y_j)^{(+)}$.

The middle case.

$$\text{II} = \left\{y: \sum_{j=1}^{r-1} (Y_j - y_j) \leq y_r < \sum_{j=1}^{r-1} (Y_j - y_j)^{(+)}\right\}$$

where $t = C_1\left(\sum_{j=1}^{r-1} (y_j - Y_j) + y_r\right) + C_2 y_r + C_3\left(\sum_{j=1}^{r-1} (Y_j - y_j)^{(+)} - y_r\right)$.

The excess bright storage case.

$$\text{III} = \left\{y: \sum_{j=1}^{r-1} (Y_j - y_j)^{(+)} \leq y_r\right\}$$

where $t = c_1\left(\sum_{j=1}^{r-1} (y_j - Y_j) + y_r\right) + C_2 \sum_{j=1}^{r-1} (Y_j - y_j)^{(+)}$.

These cost terms can be aggregated to a degree (for a particular realization of the demand variables) as:

$$S_k = C_4\left(\sum_{j=1}^{r-1} (Y_{jk} - y_j) - y_j\right)^{(+)} + C_1\left(\sum_{j=1}^{r-1} (y_j - Y_{jk}) + y_r\right)^{(+)}$$

$$+ C_2 y_r + \begin{cases} C_3 \sum_{j=1}^{r-1} (y_j - Y_{jk})^+, & \text{when } y \in \text{I} \\ C_3\left(\sum_{j=1}^{r-1} (Y_{jk} - y_j)^+ - y_r\right), & \text{when } y \in \text{II} \\ C_2\left(\sum_{j=1}^{r-1} (Y_{jk} - y_j)^+ - y_r\right), & \text{where } y \in \text{III} \end{cases}$$

We may now state the entire problem as

(1)

$$\text{minimize} \quad \sum_{k=1}^{N} p_k S_k.$$

$$y \in R_+^r$$

where k is summed over all possible realizations of the demand vector.

Because $\sum_{k=1}^{N} p_k = 1$, we may write the objective function in (1) as

(2)

$$E(y) = C_2 y_r + \sum_k p_k t_k,$$

where $t_k = S_k - C_2 y_r$.

PROPERTIES OF THE PROBLEM AND THE OBJECTIVE FUNCTION

Theorem 1: If $0 \leq C_2 \leq C_3 \leq C_1 + C_4$ then $E(y)$ is convex.

Before describing how this theorem is proved we observe that this arrangement of costs is a natural one. Since C_2 is the cost of labeling from bright storage, it is clearly less than or equal to C_3—the cost of unlabeling then relabeling which requires an extra operation.

The cost C_3 is only incurred when there is a shortage in one label and a simultaneous excess in another. If $C_3 > C_1 + C_4$ it would be better to incur the liquidation costs in one label and the short fall costs in the other, than to unlabel then relabel. (For any choice of demand vector, C_1 and C_4 will not be incurred simultaneously.)

This theorem gives a computational advantage when seeking to minimize $E(y)$ as must be done in this problem. If a local minimum is discovered it must be the global minimum as well, because of this property.

The theorem may be proved by showing that any particular term S_k is convex, then since $p_k \geq 0$ we will have that $\sum_{k=1}^{N} p_k S_k$ is convex. A straightforward but tedious procedure for showing S_K to be convex is to use the definition of convexity and apply it to $E(y)$. The details are messy and are omitted.

Consider the following linear programming problem:

$$\text{minimize } c_2 y_r + \sum_{k=1}^{N} p_k[(c_4 - c_3)z_k^+ + c_1 z_k^- - c_2 d_k^+ + c_3 d_k^-]$$

subject to:

(3)

$$y_j + u_{k,j} - v_{k,j} = Y_{k,j} \tag{3.1}$$

$$y_1 + \cdots + y_r + z_k^+ - z_k^- = \sum_{j=1}^{r-1} Y_{k,j} \tag{3.2}$$

$$u_{k,1} + \cdots + u_{k,r-1} - y_r + d_k^+ - d_k^- = 0 \tag{3.3}$$

$$y_j, y_r, u_{k,j}, v_{k,j}, z_k^+, z_k^-, d_k^-, d_k^+ \geq 0 \tag{3.4}$$

$$(j = 1,2,\ldots,r-1), (k = 1,2,\ldots,N)$$

(Note that in this formulation z_k^+ is not the same as $(f)^+$, the "plus" function of the original formulation. In this case z_k^+, z_k^-, d_k^- are variable names.)

Theorem 2: Problem (1) and problem (3) are equivalent.

Theorem 2 suggests that we can apply a well known and well tested methodology to (3) in order to find a solution to (1). The constraints 3.1-3.3 correspond to the regions I, II and III of definition of the function $E(y)$. For example, z_k^- measures the amount of overproduction across all labels. If there is no overproduction 3.4 forces z_k^- to be zero. Observe that in the objective function of (3) z_k^- is multiplied by the cost per unit of overproducing. z_k^+ measures the overall short fall for realization k. Thus it is multiplied by C_4 in the objective function. (It is also multiplied by $-C_3$ for reasons explained later.) In 3.3 $d_k^+ > 0$ this means that $u_{k,1} + \cdots + u_{k,r-1} < y_r$. Since $u_{k,j}$ measures underproduction in label j (3.1), the amount of goods to be labeled from bright storage is $y_r - d_k^+$, so that $C_2(y_r - d_k^+)$ occurs in the objective function. Finally, if $d_k^- > 0$ in 3.3, the amount in bright storage y_r is not enough to make the shortfall in each label—$u_{k,1} + \cdots + u_{k,r-1}$. Since z_k^+ measures the net shortfall (the amount of demand we will not be able to fill) $d_k^- - z_k^+$ measures the demand we can fill by unlabeling some goods, then relabeling. For each realization we will have:

$$C_4 z_k^+ + C_1 z_k^- + c_2(y_r - d_k^+) + C_3(d_k^- - z_k^-)$$
$$= C_2 y_r + (C_4 - C_3)z_k^+ + C_1 z_k^- - C_2 d_k^+ + C_3 d_k^- .$$

If each term is multiplied by p_k, and the result summed, we will have the expected cost of this choice of $y_1, \ldots, y_r$. Using the fact that $\sum_{k=1}^{N} p_k = 1$, we get the objective function of (3).

The proof of theorem 2 requires showing that (3) has a feasible point and proving two lemmas.

Lemma 1

A necessary and sufficient condition for (3) to have a solution is that $c_2 \leq c_3 \leq c_1 + c_4$.

Lemma 2

Any optimal solution of (3) computed by the simplex method will have the following complementary conditions:

$$\sum_{k=1}^{N} u_{k,j} \cdot v_{k,j} = 0 \qquad (j - 1, \ldots, r - 1)$$

$$\sum_{k=1}^{N} z_k^+ \cdot z_k^- = 0$$

and

$$\sum_{k=1}^{N} d_k^+ \cdot d_k^- = 0.$$

The strategy of the proof is to formulate the dual linear program corresponding to (3) and to use it and lemma 2 to bound solutions to (2) and (3). Lemma 1 and theorem 1 ensure that (3) will have a solution if and only if (2) has a solution. It can then be shown that an optimal solution for (2) also is optimal for (3) and vice versa.

Theorem 2.

If all realizations Y_k $(k = 1, \ldots, N)$ are integer vectors and $c_2 \leq c_3 \leq c_1 + c_4$, then there exists an integer optimal solution for the bright storage problem (1).

Besides getting rid of annoying cases where the best solution may be to label half a container, this theorem may help in computational matters associated with some of the very large problems that can result from a real application of these methods. It's proof requires showing that the determinant of the linear programming basis matrix at any intermediate step in the simplex method is always $\pm$ 1. The details are messy and they are omitted.

COMPUTATION

The LP formulation contains a large number of variables for practical sized problems. If $r - 1$ is the number of labels and n is the number of realizations of the Y_k vector, the number of constraints is given by

$$N \cdot (r + 1)$$

and the number of variables by

$$2 \cdot N \cdot (r + 1) + r.$$

Initial computational experiments have been conducted for an example problem with two labels and six realizations. The purpose of the experiments was to determine the effect of changing the costs on the optimal amount of bright storage required. Other experiments were conducted in an attempt to discover how different distributational assumptions for y, affected the solution.

The first set of costs $C_1 = 3.0$, $c_2 = 1.0$, $c_3 = 1.5$ and $C_4 = 4.0$, produced a solution requiring no bright storage for every associated distribution used. We speculate that if the costs for unlabeling-relabeling (C_3) are near the costs for labeling from bright storage (C_2)

then it is better to label all the containers, because adverse consequences of labeling too many for a particular brand are not pronounced. When the value of C_3 was increased ($C_3 = 5$) for the same distributions with other costs remaining constant there were still distributions which produced optimal solutions with no bright storage. However, some of the solutions did require bright storage and some of these were unique solutions to (3).

Further tests were conducted at Madison Academic Computing Center, using a Univac 1100 series computer and Univac's FMPS mathematical programming software (1974). This allowed the testing of some larger problems. The same patterns as reported above were detected again. In a large number of cases, where there was only a small difference between the per unit shortfall cost and the unlabeling-relabeling alternative, the optimal solution generated required no bright storage. In cases where this difference increased the optimal solution generated tended to require bright storage. Computing time for a three label problem with 60 realizations of the joint probability distribution was approximately 14 s. I7 every example attempted, a starting basis consisting of the z_k^+, d_k^- and u_r variables was specified. In this circumstance the number of iterations was approximately equal to the number of rows in the constraint matrix.

CONCLUSIONS

Much work has to be done before large bright storage problems can be solved easily. If historical demand data are used to generate distribution information about the realizations, one hundred or more realizations per variable may be warranted. Because of the large size of the implied linear program, a streamlined solution technique seems to be required. Other factors are the impact of independence (or lack of it) of the demand variables on the nature of the solution and the impact of using discrete approximation for continuous distributions assigned to the demand variables.

ACKNOWLEDGMENTS

We would like to acknowledge the helpful suggestions from the referrees. This research was supported by the College of Agricultural and Life Sciences, University of Wisconsin-Madison, Madison, Wisconsin.

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LITERATURE ABSTRACTS

ABSTRACTS FROM JOURNAL OF FOOD SCIENCE

KINETICS OF THIAMIN AND RIBOFLAVIN LOSS IN PASTA AS A FUNCTION OF CONSTANT AND VARIABLE STORAGE CONDITIONS. *J.F. Kamman, T.P. Labuza and J.J. Warthesen. J. Food Sci.* **46,** *1457-1461.*

The stability of thiamin and riboflavin in enriched pasta humidified to different water activities was measured at 25, 35, 45, and 55°C. for periods of up to 1 yr. Riboflavin was shown to be extremely stable (dark reaction) whereas thiamin losses were significant. Thiamin loss increased with temperature (Q_{10} of 4.5) and water activity. Predictions of thiamin loss for a square wave temperature fluctuation using steady state data were compared to actual losses found in storage for pasta held at equal alternating times at 25/45 and 25/55°C. The Hicks-Schwimmer-Labuza model provided an adequate method for predicting both the amount of loss and the effective temperature from steady state data.

ANALYSIS OF PROPAGATION OF FREEZING AND THAWING FRONTS. *Y. Talmon and H.T. Davis. J. Food Sci.* **46,** *1478-1483 + 1488.*

The modified isotherm migration method (MIMM) is used to calculate the temperature profiles and freezing (thawing) times for symmetrically cooled (heated) slabs with meat-like thermal properties. MIMM, which is reviewed briefly is not restricted to the usual idealizations such as zero surface resistance, uniform critical temperature distribution, and infinitely large sample. Dimensional analysis is used to identify the dimensionless groups controlling freezing and thawing front propopation in slabs, cylinders, and spheres having uniform thermal properties and constant freezing temperature. The MIMM results provide a basis for evaluating the qualitative origins and the quantitative extent of the sucess of Plank's (1913) old model. The freezing times predicted by the moving front model used here agree with those predicted by the empirical correlation found by Cleland and Earle for the Karlsruhe test substance.

CORRECTION FACTOR OF COME-UP HEATING BASED ON MASS AVERAGE SURVIVOR CONCENTRATION IN A CYLINDRICAL CAN OF HEAT CONDUCTION FOODS. *J. Uno and K. Hayakawa. J. Food Sci.* **46,** *1484-1488.*

A mathematical expression is derived to estimate a correction factor for come-up heating which may be used to calculate mass average survival concentrations. For this derivation, analytical heat conduction formulae are used to estimate transient state temperature distributions in a cylindrical can of heat conduction food. Through the dimensional analysis of the derived analytical expression, 12 dimen-

sionless groups are formulated in order to examine the influence of various process conditions as well as of food properties on the correction factors. Theoretical correction factors are then computed for various numerical combinations of these dimensionless groups. Through the nonlinear regression analyses of these computed factors, we obtain algebraic equations for representing these factors as a quadratic function of the dimensionless groups. There is fair agreement between the correction factors estimated by using the algebraic equations and by using heat penetration data collected experimentally.

CORRELATIONS OF ENTHALPIES OF FOOD SYSTEMS. *H.D. Chang and L.C. Tao. J. Food Sci.* **46**, *1493-1497.*

Correlations of enthalpies of food systems containing water fraction from 0.74-0.94 are presented for a temperature range 230-310°K (-50 to 95°F); with these correlations, energy requirement in freezing and thawing foods within the limits of data base used for this work may be computed by providing the identity of food group (meat, juice or vegetable/fruits), water content, initial, and final temperatures.

PILOT PLANT PRODUCTION OF AN EDIBLE ALFALFA PROTEIN CONCENTRATE. *R. Fiorentini and C. Galoppini. J. Food Sci.* **46**, *1514-1517 + 1520.*

This paper reports the development of a pilot plant scale wet fractionation process to obtain an edible leaf protein concentrate from alfalfa juice by the fractionated recovery of the chloroplastic and cytoplasmatic proteins. The green pigmented fraction is recovered at room temperature by employing an organic polyelectrolyte, while the edible white proteins are coagulated by acidification to pH 4.0. The pilot plant and working conditions are described together with the chemical composition of the final products. Some functional properties of cytoplasmatic protein concentrate are also reported. Since the whole process takes place at room temperature the cytoplasmatic protein concentrate shows good functional properties especially with regard to its nitrogen solubility.

CARROT DEHYDRATION-OPTIMIZATION PROCESS STUDIES ON THE EXPLOSION-PUFFING PROCESSING. *J.F. Sullivan, R.P. Konstance, E.S. Dellamonica, W.K. Heilland and J.C. Craig Jr. J. Food Sci.* **46**, *1537-1542.*

A carrot dehydration process that includes the unique continuous explosion-puffing system (CEPS) is described. A drying study included moisture distribution throughout a two-stage pilot scale dryer as well as bed temperature during first stage drying. Shrinkage losses of carrots by two dehydration methods were investigated, and volume differences were obtained. Measurements of dried carrot properties such as bulk density, color, nonenzymatic browning, rehydration, and disintegration were used to determine optimum operating pressure, temperature, and feed moisture for CEPS. Response surfaces developed from these properties were used simultaneously to establish a constrained optimum.

EFFECTS OF INSULATION ON THE EXTENT OF FREEZING OF TOMATO PRODUCTS STORED IN ASEPTIC BULK STORAGE TANKS. *M.C. Dale, D.R. Lesley, M. Okos and P. Nelson. J. Food Sci.* **46**, *1546-1551.*

A finite difference model was developed to determine the effects of insulation on the extent of freezing of tomato puree stored in aseptic bulk storage silos exposed to winter weather conditions. The model was validated using data obtained from the freezing and thawing of a small cylinder of tomato purée. Density, heat capacity, and thermal conductivity were written as functions of temperature, percent solids, and percent ice fraction. Storing high percent solids of a small amount of insulation could greatly reduce the extent of freezing in a silo. Three inches of foam type insulation were sufficient to prevent freezing of 8.5% solids tomato puree for a severe winter (1979) in the northeastern region of Indiana using temperatures and wind speeds collected by the Ft. Wayne, IN weather station. One inch of insulation was sufficient to prevent freezing in 21% solids tomato puree.

STRUCTURAL COLLAPSE AND VOLATILE RETENTION DURING HEATING AND REHUMIDIFICATION OF FREEZE-DRIED TOMATO JUICE. *L.N. Gerschenson, G.B. Bartholomai and J. Chirife. J. Food Sci.* **46**, *1552-1556.*

The effects of temperature, moisture content, and pectin addition on the "collapse" of freeze-dried tomato juice cake and retention of volatiles were investigated. High temperatures and high moisture contents induce collapse and the loss of volatiles, which was measured with ^{14}C-labelled butyl acetate. The addition of pectin, which enhances the viscosity of the tomato juice, increases its "collapse" temperature after freeze-drying and the retention of volatiles.

MOISTURE MIGRATION IN FROZEN, RAWBREADED SHRIMP. *S.K. Williams, R. Martin, W.L. Brown and J.N. Bacus. J. Food Sci.* **46**, *1577-1581.*

The extent of moisture migration from the flesh of frozen, raw breaded shrimp was studied fro 9 months. The experiments were designed to monitor the effects of moisture migration on the total net weights and the total "percent shrimp material." The breaded shrimp were (1) blast frozen-stored in the retail freezer (-16°F, -26.6°C). (2) blast frozen-stored in the warehouse freezer (-12°F ± 2°, -24.4°C), (3) individually quick frozen (IQF)-stored in the retail freezer (-16°F, -26°C), and (4) individually quick frozen stored in the warehouse freezer (-12°F ± 2°, -24.4°C). As storage time increased the precent breading increased for all treatments. The percent shrimp, the gross weights, the net weights, and the percent moisture decreased as storage time increased. The rate of moisture migration was retarded in the breaded shrimp (i.e. IQF and blast frozen) stored in the warehouse freezer, when compared to the rate of moisture migration in the breaded shrimp (i.e. IQF and blast frozen) stored in the retail freezer.

FISH ORIENTATION AND FEED RATE EFFECTS ON AIR SEPARATION BY SHAPE. *R. Carey, L.F. Whitney and L.R. Correa. J. Food Sci.* **46**, *1582-1585.*

A mechanical system has been developed to automatically separate flat fish from round fish by utilizing their differences in projected area and aerodynamic properties. A continuous stream of mixed fish is moved along a belt conveyor at a rapid rate, and upon discharge each fish is subjected to a blast of high velocity air. Differences in shape and ratio of projected area to weight of flat fish and round fish are sufficient to alter their trajectories and therefore enable their separation. Experimental results indicate that the system is a practical method to sort fish by shape, either at sea or ashore.

STABILITY OF PROTEINS IN ULTRAFILTERED, LOW-LACTOSE MILK CONCENTRATE DURING FROZEN STORAGE. *O. Fennema and C.H. Amundson. J. Food Sci.* **46**, *1603-1611.*

Casein in concentrated milk (3X) destabilizes after 1-3 wk at -8°C. Use of an ultrafiltration (UF) process to partially remove lactose from milk, followed by replacement of all or part of the removed lactose with corn syrup, glucose or sucrose can greatly extend protein stability. Protein stability improves as the amount of nonlactose carbohydrate is increased and the amount of lactose is decreased. Although nutritionally significant amounts of minerals and vitamins are removed by this process, they can be easily replaced. Samples of skim and whole milk from which 68-72% of the lactose is removed by UF and replaced on an equal weight basis with corn syrup are stable for more than 34 wk at -3°C.

ON THE WATER ACTIVITY OF LACTOSE SOLUTIONS. *J.L. Miracco, S.M. Alzamora, J. Chirife and C. Ferro Fontan. J. Food Sci.* **46**, *1612-1613.*

The water activity of aqueous lactose solutions up to about 17% (w/w) (saturation at 25°C) has been determined from measured freezing points. As expected, results agree well with Raoult's law and do not substantiate some literature results which attributed considerably lower water activity values to lactose solutions.

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HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57,* 142—147.

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