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### **Apricot Breakdown**

### A Quality Defect in Canned Apricots

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In 1958 it was first reported that fruit in some batches of canned apricots were softening and breaking down within a few months of processing. This disorder has been detected in some of each season's production since 1958 and has seriously affected the marketing of this attractive product.

Apricot 'breakdown' results in a slow loss of integrity of apricot halves and occurs in some cans of fruit within several months of processing. When the cans are opened the fruit still appear as intact halves, but with substantial loss of shape, so that they tend to collapse into a cloudy syrup. In severe cases the fruit may be completely disintegrated, resembling a purée. The degree of breakdown depends upon time and temperature of storage and the amount of agitation the cans have received. In contrast, the desirable product consists of well-formed apricot halves in a clear syrup, which retain a firm cup shape no matter how much handling the can has had (see illustration on page 34).

In Australia the disorder has been observed only in apricots (mainly Trevatt variety) grown in the Murrumbidgee Irrigation Area of New South Wales (M.I.A.), which are canned locally or transported some distance for canning. Since the first report the disorder has appeared every season, but to a varying extent, so that it is difficult to assess the losses involved. An indication of its importance can be gained from the fact that one cannery, which currently processes about 500 tons of apricots annually, has, over the past few seasons, lost about one-third of its production of apricots canned in syrup as a result of breakdown. The important export trade in canned apricots has been affected and this, in turn, has had the wider effect of prejudicing importers against Australian canned fruit.

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#### Nature of the Disorder

Closer inspection of affected apricots shows that the tissue has lost its cohesiveness, so that when touched, the skin breaks readily and separates from the flesh, which falls apart. The condition is shown clearly by two empirical tests that have been applied to assess breakdown. In the 'pinch' test, the skin is pinched between the thumb and first finger and an attempt is made to lift the apricot half. When breakdown has occurred the skin tears and pulls away from the flesh so that the apricot falls some distance or, in severe cases, cannot be picked up. The second test, known as the 'plop' test, is based upon the fact that if an attempt is made to pick up such a half by placing the thumb into the cup of the fruit and the first finger on the outside, the fruit will break in two and 'plop' back into the dish.

The breakdown condition described here is to be distinguished from that of canned over-mature apricots which tend to lose their cup shape, although the skin and flesh remain intact and the fruit can be handled without disintegrating. It is also different from the loss of firmness to which some varieties are subject and which is apparent immediately after processing. Microscope examination of apricots showing breakdown reveals that the cells have separated, presumably owing to dissolution of the pectin of the middle lamella which binds the cells together. This view has been confirmed by chemical analysis which shows a loss of insoluble protopectin and an increase in soluble pectin compared with unaffected canned apricots.

Breakdown in the can is usually a slow



Canned apricot halves (*left*) showing breakdown and (*right*) normal.

process, taking up to six months to become obvious at normal warehouse temperature. However, it may often be detected earlier by the 'pinch' test since skin fragility appears to be one of the first symptoms.

#### **History of Investigations**

Since the first reports of the disorder in 1958 a considerable amount of cooperative work has been carried out by this Division, the New South Wales Department of Agriculture, and the canneries concerned. The Irrigation Research and Extension Committee of the Murrumbidgee Irrigation Area and the Australian Canning Fruits Advisory Committee have been deeply concerned. A subcommittee of the Committee for the Coordination of Fruit and Vegetable Processing Research in New South Wales was established to coordinate investigations on this disorder. Under the auspices of these bodies a series of research programmes has been undertaken since 1958 to study a large number of possible factors.

#### Agronomic Conditions

Early work concentrated on the study of cultural conditions that might possibly be involved. The following factors were investigated without any definite relationship being established: nitrogen and phosphorus fertilizer levels and time of application, irrigation in relation to tree moisture stress, soil type and condition, and health and age of the trees. Likewise, temperature at harvest and maturity and size of fruit at harvest showed no correlation with breakdown, nor could processing conditions, e.g. exhaust time, and temperature and length of cook, be linked with the disorder.

#### Fungal Contamination

Canned apricots showing breakdown were examined for the presence of Byssochlamys spp., a fungus which forms heat-resistant ascospores, capable of growth in an acid medium such as apricots, and which has caused similar disorders in other canned fruits (Hull 1939). No evidence of growth by this organism could be found in any of the material examined. More recently, when a similar breakdown problem in South Africa was attributed to the growth of B. fulva in canned apricots (Stellenbosch Fruit and Food Technol. Res. Inst. 1969), the question was re-examined, but again with negative results. Moreover, the disorder could not be reproduced by inoculating cans with *Byssochlamys* of known heat resistance.

#### Macerating Factor

When breakdown occurs, the entire contents of the can are usually affected and only rarely, during the early development of the disorder, do some halves show breakdown while the remainder are firm. This observation makes it unlikely that the disorder arises because of textural weakness in individual fruit and points rather to the presence of a 'macerating factor' which affects all the fruit in the can.

The factors most likely to affect such a uniform change in fruit structure are hydrogen ion concentration and enzyme activity. Either low or high pH could cause abnormal texture changes (Doesburg 1965) and breakdown in some samples of canned apricots in California has been correlated with pH below 3.55 and high acidity (Luh and Dastur 1968). However, extensive surveys of Australian canned apricots failed to reveal any such relationship, most of the packs showing breakdown having pH in the range 3.8-4.0.

Enzymes are normally inactivated during the heat processing of canned fruits. Therefore, it first appeared unlikely that the disorder was caused by survival of enzymes especially since not all canned apricots were affected and breakdown has only been reported since 1957/58. This view was supported when enzyme activity could not be detected in canned apricots showing breakdown. However, field observations suggested that occurrence of the disorder might be associated with contamination of sound fruit by rotting fruit which is difficult to avoid during transport, storage, and ripening. It was thought possible that enzyme activity in the rotting material might cause some weakening in the skin of contaminated sound fruit, thus allowing chemical degradation of the pectin to proceed more rapidly in the canned product.

Consequently a number of experiments were carried out in which apricots were smeared with a purée made from over-ripe and rotting apricots, allowed to stand for some time, then washed and canned. Although the results were variable, there was some success in inducing typical breakdown by this method, but the experiments seemed unrealistic in that the amount of contamination found necessary would not occur in practice. Subsequently, it was found that the mere addition of some of the 'leak' or exudate from rotting apricots to the can immediately before closing was sufficient to cause the apricots to break down after several months of warehouse storage.

The conclusion drawn from these observa-



Typical 'nest' in fresh apricots due to growth of the mould *Rhizopus nigricans*.

tions was that fruit which rotted as a result of microbial growth produced a 'macerating factor' capable of surviving the canning process.

#### **Present Investigations**

Transit rot, caused by *Rhizopus nigricans*, is probably the most common post-harvest disease in stone fruit causing much of the rot and 'leak' previously described (Jenkins 1965). Typically, the mould forms a white mycelial mass which bears black spore bodies and spreads into adjacent fruit forming nests of rotting fruit, as illustrated on this page.

This fungus appeared to be a likely source of the 'macerating factor'. When grown on stone fruit, *R. nigricans* produces a strong pectolytic enzyme system which breaks down the tissue forming the 'leak' which is strongly pectolytic and rots healthy fruit that it touches.

Trials over two seasons have now shown conclusively that infecting apricots from the M.I.A. with *R. nigricans* can cause subsequent breakdown of the canned product. Treating infected fruit with dichloran (2, 6-dichloro-4nitroaniline), a fungistat effective against *Rhizopus* spp., has reduced the development of the infection and also the amount of breakdown. Furthermore, the 'leak' produced by growing *R. nigricans* on M.I.A. apricots has been found to contain a pectolytic enzyme so heat-stable that activity can be detected after it has been boiled for 16 minutes (Harper 1971).

It is concluded, therefore, that the growth of R. nigricans on apricots during storage and transport may contribute to breakdown, the breakdown being caused through production of a thermo-stable pectolytic enzyme. This enzyme dissolves the pectin of the middle lamella so that cells separate and the tissue slowly loses its integrity during storage.

However, this theory does not appear to answer all questions that might be asked. For instance, why does breakdown sometimes occur in apricots showing no signs of *Rhizopus* infection at the time of canning? Why is breakdown encountered only in fruit grown in the M.I.A.? Why has it become a problem only since 1958, when *Rhizopus* has always been a common pathogen in the fruit-growing areas of Australia?

The first question has been answered by studies which have shown that the enzyme necessary for the fungus to progress through the fruit is formed in sufficient quantity to cause the damage during the early stages of infection. This happens before the mycelium becomes externally visible, and therefore absence of visible mould on the apricots is no guarantee that they will not break down after canning.

The second and third questions are, as yet, unanswered, but current work is aimed at providing further evidence that *Rhizopus* infection is the primary cause of breakdown in commercial canned apricots and at throwing some light upon these other interesting anomalies.

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# Some Solubility Relationships of Limonin

#### Their Importance in Orange Juice Bitterness

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This article is based on a talk given at the Tenth Symposium of the Scientific and Technical Commission of the International Federation of Fruit Juice Producers, Palermo, Sicily, April 1970, and published in the reports of that symposium.

During work on the problem of bitterness in processed orange juice, difficulty has been experienced in preparing stable, intensely bitter, aqueous solutions of the bitter principle, limonin. Although limonin is extremely insoluble in water, it is responsible for the development of objectionable bitterness in orange juice, and intensely bitter solutions might be expected from refluxing limonin with water, provided the pH was adjusted to below  $4 \cdot 5$  to prevent the hydrolysis of limonin to the non-bitter ion of its hydroxy acid form.

However, such procedures do not work, and the simplest way to prepare intensely bitter aqueous solutions of limonin is to dissolve it in alkali or an organic solvent such as acetone or alcohol and to add this solution to boiling acidified water. The solutions so obtained are probably colloidal and not true solutions of limonin. Thus, the bitterness in these preparations declines with varying rapidity from objectionably intense to moderate levels in a few days under conditions that inhibit limonin autoxidation, indicating the physical instability of the solutions.

#### Solubility of Limonin

The development of a method for limonin assay (Chandler and Kefford 1966) made possible a closer study of this problem. Aqueous solutions prepared by refluxing powdered crystalline limonin with water, acidified to pH 3.2 with citrate buffer, had limonin contents of the order of 10 p.p.m., in contrast to the highest concentration reached in freshly processed Navel orange juice of about 45 p.p.m. Thus, even though concentrations of 50 p.p.m. could be achieved in a refluxing solution, as Table 1 shows,

Table 1

Solubility of Limonin (p.p.m.) in Water under Reflux (3 hr)	(pH 3·2)
Solution filtered, hot	50
Solution filtered, cooled	16
Solution filtered after 2 days at 25°C	10
Solution filtered after 8 days at 25°C	6

limonin rapidly passed out of solution on cooling. After standing a few days the solution was therefore only slightly bitter, whereas processed Navel orange juices remain intensely bitter over long periods of storage.

To elucidate the reason for this discrepancy, an attempt was made to simulate the conditions that exist in normal processed orange juice. Limonin was added to model aqueous solutions, acidified to pH  $3 \cdot 2$  with citrate buffer, in lacquered cans, and the cans were closed and either retorted for 1 hr or spin-cooked in steam for 1 min; before analysis, the solutions were treated with Celite (3 g/100 ml) and passed through a fine sintered-glass filter. Because compounds in the crystalline state tend to resist solution, these experiments used amorphous limonin prepared by addition to water of concentrated solutions of limonin in acetone.

Table 2 Solubility of Limonin (p.p.m.) in Retorted Solutions (1 hr)

(,		
Solution		10% Sugar (pH 3·2)
Filtered, hot	48	220
Filtered, cooled	21	62
Filtered after 2 days at 25°C	17	26
Filtered after 8 days at 25°C	13	18

#### Effect of Sucrose

A comparison of the results obtained with retorted solutions using water and a 10%sucrose syrup is given in Table 2. With water, the retort process gave similar results to the reflux treatment, although limonin tended to remain in solution for longer periods in the cans, possibly because glass vessels used for refluxing offered more centres for crystallization of limonin. Addition of 10% sugar, however, caused a fourfold increase in the solubility of limonin in the hot retorted solution, although limonin passed out of solution rapidly on cooling and eventually the concentrations with and without sugar differed only slightly.

When the cans were spin-cooked, the results shown in Table 3 were obtained. In water, only small amounts of limonin passed into solution, and since most of this came out of solution after 8 days, it is apparent that under equilibrium conditions at 25°C very little limonin indeed would remain in solution. The presence of sugar again increased the solubility, but the levels were much lower

Table 3 Solubility of Limonin (p.p.m.) in Spin-cooked Solutions (1 min)

Solution		10% Sugar (pH 3·2)		
Filtered, hot	8 (48*)	20 (220*)		
Filtered, cooled	8	20		
Filtered after 4 hr at 25°C	7	18		
Filtered after 2 days at 25°C	4	16		
Filtered after 8 days at 25°C	2 (13*)	10 (18*)		

\* Comparable figures for retorted solutions.

than in retorted solutions owing to shorter heating periods, and clearly under equilibrium conditions there would be less than 10 p.p.m. limonin in solution, since the concentration was still falling up to the eighth day of storage when this value was recorded.

#### Effect of Pectin

Obviously some factor other than sucrose contributes to the solubilization of limonin in orange juice to the point of intense bitterness, and from the results in Table 4 pectin

#### Table 4

Effect of Storage on Solubility of Limonin (p.p.m.) in Model Systems (pH 3·2) Solutions prepared under reflux

Storage	10% Sugar	0.1% Pectin	10% Sugar 0·1% Pectin
1 hr		80	87
2 days	18	43	63
8 days	18	22	32
16 days	15	18	28

seems to be this factor. These results show that addition of 0.1% pectin greatly increased the solubility of limonin in aqueous solutions prepared under reflux so that, even after several weeks, the solutions retained sufficient limonin for them to taste bitter, and the presence of sugar in the pectin solution increased its solubility in stored solutions even further.

The effect of varying pectin concentrations on limonin solubility in 12% sucrose syrup was then measured over extended periods, and so was the similar effect of varying sugar contents in solutions of constant pectin concentration. The model systems were adjusted to pH 3.2 with citrate buffer to give a 1% titratable citric acid content, and spin-cooked in cans with amorphous limonin under conditions closely resembling the commercial process for orange juice. As before, solutions prepared by spin-cooking in cans retained their state of supersaturation longer than comparable solutions prepared by refluxing in glass vessels.

Table 5 gives the result of varying pectin contents on the solubility of limonin in 12%sucrose syrup. Apart from a few slight

	Table 5
Effect	of Pectin Content on Solubility of Limonin (p.p.m.) in 12% Sucrose Syrup (pH 3·2)
	Solutions prepared by spin-cooking

Storage	P	ectin C	ontent	(% w/	w)
(wk)	0	0.02	0.05	$0 \cdot 1$	0.2
1	36	41	51	60	77
2	31	28	46	43	42
4	18	24	23		40
9	14		20	31	45
12	14	18	20	28	40

anomalies, the data demonstrate that addition of 0.2% pectin to 12% sugar solution increases the solubility of limonin about threefold, and this could result in intensely bitter solutions that are stable for several months. In this particular run, a steady state was reached after one to two months at the five levels of pectin content, with limonin concentrations increasing with increasing pectin content. This result was reproducible; although the period required for equilibration varied, the limonin concentrations at each pectin content remained about the same.

The results of the associated experiment, varying the sugar content in solutions of constant pectin content, are shown in Table 6. Despite some anomalies, notably an apparent rise and fall in limonin solubility in the solutions containing no sucrose, it is obvious that variations in sugar content have less effect on limonin solubility in pectin solutions than variations in pectin content have on limonin solubility in sugar solutions. In 12%

Table 6 Effect of Sugar Content on Solubility of Limonin (p.p.m.) in 0.1% Pectin Solutions (pH 3.2)

Solutions prepared by spin-cooking

Storage	Su	crose C	Content	(% w/	w)
(wk)	0	3	6	12	15
1	28	24	35	42	45
2	28	35	37	39	35
5	39	42	41	42	38
9	42	39	47	45	40
11	40	43	45	34	38
20	28	47	40	28	33
30	30	22	29	27	28

sucrose syrups limonin concentrations, determined after certain periods of storage, ranged from 14 to 77 p.p.m. according to pectin content with about one value in three falling below 25 p.p.m.; with 0.1% pectin solution, such concentrations ranged from 22 to 40 p.p.m. with only one value in thirty falling below 25 p.p.m.

#### Discussion

The results of these experiments suggest that the main effect of sugar is to increase the solubility of limonin at high temperatures, while the effect of pectin is to hold it in solution after cooling. The combined effect of pectin and sugar is to create and maintain in the system conditions that may lead to high limonin concentrations. Consequently orange juice, which contains approximately 10% sucrose and 0.1% pectin, is able to maintain limonin contents high enough to taste objectionably bitter, provided there is enough limonin in the original fruit to produce such concentrations in the juice. It is interesting to consider that but for the effect of pectin and sucrose in increasing the solubility of limonin in aqueous systems, there would be no such problem as bitterness in orange juice.

A number of independent observations support the above conclusion. Firstly, cans of immature Navel juice which had been stored in these laboratories for about 15 years at 0°C have deposited hard, sandy crystals about the size of commercial cane sugar (see illustration). This has been shown to be practically pure limonin which had apparently come out of solution during long storage of the juice. The reason for this loss of solubility is now seen to be loss of pectin from the juice as a result of acidic hydrolysis during storage. Although no pectin analyses were carried out, the failure of the juice to hold its pulp in suspension for more than a few seconds indicated considerable degradation of pectin during the 15-year period.

Furthermore, a scientific basis is now provided for several procedures that have been suggested, on empirical grounds, as practical ways to debitter citrus juices containing limonin. Over 20 years ago Russian workers, unaware that they were concerned with limonoid and not flavonoid bitter principles such as naringin, reported the removal of bitterness from tangerine and other citrus products by the simultaneous addition of peroxide and peroxidase preparations from apples (Markh and Fel'dman 1949, 1950; Markh 1953). It seems likely that the effectiveness of this process depended on pectic enzyme impurities in the crude peroxidase preparations.



Limonin crystals deposited in Navel orange juice on prolonged storage.

At about the same time, the U.S. Department of Agriculture reported that pectolysing enzymes from fruits or fungi were capable of debittering orange juice after several hours at  $4-10^{\circ}$ C (McColloch 1950; Anon. 1951). It was suggested that such enzymes, naturally present in unpasteurized Navel orange juice, were involved in the slow loss of bitterness from this product on storage at 3°C. The process was not further studied because it was associated with off-flavour development and loss of cloud, but the decrease in bitterness was believed due to a disruption of the colloidal conditions that held limonin in solution, rather than to disruption of the limonin molecule itself.

The suggestion was made recently by the author (Kefford and Chandler 1970) that the reduction in limonin concentrations by enzymes from Aspergillus and Penicillium moulds (Nomura 1966) could be due to residual pectinase activity. However, details of this work, not then available, reveal that solubility relationships could not account for these results which may, on the other hand, be related directly to recent reports of degradation of limonin by soil bacteria (Bennett, Hasegawa, and Maier 1971). In addition, the presence of limonin-degrading enzymes in orange albedo has been demonstrated (Kefford and Chandler 1970; Flavian and Levi 1970) under conditions which avoid confusion of the effect of such enzymes with the effect of pectinases on limonin solubility in pectincontaining systems.

In a recent British patent (Hanson and Salada Foods 1968) for the preparation of a non-bitter Navel concentrate, one of the steps is to heat the extracted juice with an enzyme system high in pectinesterase activity and low in pectin polygalacturonase activity. It is claimed that this procedure counteracts the formation of bitter substances as well as giving a juice of low viscosity which is easier to concentrate. Solubility studies reported above indicate that the function of the pectic enzymes is not to counteract the formation of bitter substances but to decrease the solubility of limonin in the juice.

Finally, reference can be made to a recent development in Australia which is interesting from the general viewpoint of fruit juice technology as well as for its relevance to the solubility relationships of limonin. For several years, Australian soft drink manufacturers have been granted a rebate of sales tax on products that contain 5% fruit juice. Originally this concession was granted with the aim of promoting the utilization of citrus fruits, but apple juice processors were quick to seize upon it as a means of increasing the sales of their product. In most seasons apples are in glut supply, and a bland apple juice concentrate prepared without recovery of volatiles has been used by most soft drink manufacturers as the cheapest way to earn the sales tax rebate. Lately, however, Navel orange juice has been as cheap as apple juice, and application of the above principle has led to the production of a non-bitter Navel serum concentrate by treatment of the extracted juice with pectolysing enzymes before concentration. Centrifuging after enzyme treatment removes not only limonin, but also colour and cloud to give a clear serum of low viscosity that is readily concentrated. The commercial preparation of this bland Navel orange juice concentrate and its use by beverage manufacturers provide a practical demonstration of the importance of the solubility relationships of limonin in the problem of bitterness in orange juice.

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# Recent Advances in Dehydration Processes

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This article is based on a talk given by the author to the AIFST Southern Section Symposium, 'Selected Aspects of Dehydrated Foods', at Clunies Ross House, Melbourne, July 8, 1970.

It took two world wars to bring about major advances in the drying of foods. Thus initiated, the last 25 years have seen drying technology attain a high degree of sophistication, resulting in products that are accepted in ever-increasing quantities in retail markets, in army logistics, and even in space travel. However, sun-drying still accounts for the major tonnage of dried foods consumed in the world today. For example, 1175 million tons of grain with rice as the principal commodity, 110 million tons of oil seeds with soya beans at 41 million tons, 34 million tons of dried legumes, and 68 million tons of coffee, cocoa, and tea are produced by use of the sun's energy as the main drying force. In most cases these materials are fully or partly dried while they are still attached to their plants in the field. Raisins, figs, and dates which total about 10 million tons are harvested before final sun-drying. Dehydrated foods are produced in small amounts compared with those mentioned above but quantities are rising rapidly.

While sun-drying is older than recorded history, dehydration is limited almost to the twentieth century and the effort put into this method of preservation in the last 25 years has been very great. Nevertheless, most of the new dehydration procedures that will be outlined here have not been fully implemented commercially.

#### **Principles of Drying**

Before describing specific methods of drying, the principles involved will be briefly summarized. The problem is basically one of heat and mass transfer. Energy must be supplied to vaporize water or sublime ice and the resultant vapours must be removed from the drying environment.

The amount of heat needed to vaporize water depends upon the temperature at which vaporization occurs. For example, at atmospheric pressure the latent heat of vaporization of water at  $212^{\circ}$ F is 971 Btu/lb and the latent heat of sublimation is 1220 Btu/lb. These values are for no loss of energy, but in practice efficiencies are well below 100%, usually in the range 20–50%. At 50% efficiency about 2000 Btu must be supplied to vaporize 1 lb of water, while at 20% the energy requirement is nearer 5000 Btu/lb.

The general equation for heat transfer is

$$q = h_s A(t_a - t_s),$$

where q is the heat transfer rate in Btu/hr,  $h_s$  is the heat transfer coefficient, A is the area,  $t_a$  is the air temperature, and  $t_s$  the temperature of the drying surface.

Conduction, convection, and radiation all occur in drying but, depending on the method used, one-dominates to such an extent that its influence is over-riding.

A current of air is the most common medium for transferring heat to a drying food and convection is the main principle involved. Air streams readily carry water vapour away from the drying surfaces and in practice, water vapour removal is seldom a limiting factor during this type of drying, as air speeds from 600 to 1000 linear feet per minute are usually employed.

Conduction and radiation assume more importance in vacuum and freeze drying, radiation being used more in recent years. In these procedures, water vapour is condensed on a cold surface leaving only noncondensible gases to be handled by pumps. Water is readily available at the surface of drying foods only in the first few minutes of the process when a short constant-rate drying period may occur. Thereafter, migration of water to the surface follows and diffusion becomes rate limiting. This results in the falling-rate period of drying which in the later stages can be exasperatingly slow. Particle size, therefore, is important in determining overall drying time. Halved or whole fruits may take 24 hours to dry while minute droplets of liquid dry in a matter of seconds.

It is in the later stages of drying that heat damage is most likely since the temperature of the product gradually rises as the drying rate falls and evaporative cooling decreases. Thus, most drying processes contain stages commencing with high temperatures and gradually falling to levels at which deterioration due to heating is minimal.

The biochemical and biophysical characteristics of individual foods define what type of dehydration procedure may be applied without causing deteriorative changes in flavour, texture, and colour—or rather, keeping such changes to levels where they are not objectionable to the consumer. In a few cases, a food may become more acceptable after drying. Today, many drying procedures are tailor-made to suit a particular food.

Heat transfer in to the point where drying is occurring and mass transfer of water out to the surface take place simultaneously and each affects the other to some degree. However, practice has already shown that design of driers and their operation can be based on calculations in which each transport factor is considered independently.

#### Types of Drying

#### Tray, Tunnel, or Belt Drying

In each of these driers food is spread in thin layers on trays or on a belt. Trays may remain stationary in a cabinet or be placed on a multi-tiered truck progressing intermittently through a tunnel; belt driers usually have only one level moving continuously through a tunnel. These common driers are versatile, permitting the dehydration of a wide range of particulate foods.

In cabinet and belt driers through-bed air flow is usual, while in tunnels cross-bed flow is almost universal. In all types uniformity of air flow is essential to ensure even temperature and uniform drying. In tunnels, drying may be counter- or parallel-flow depending upon the direction of air flow relative to movement of the trucks. More efficient drying is obtained by the centre-exhaust system where flow is parallel in the primary stage and counter in the secondary. Recirculation of part of the used air stream is general to conserve heat and raise efficiency.



Fig. 1.—Fluidized-bed drier.



Fig. 2.—Belt-trough drier. Fan and heater in rear, drying bed in foreground.

Probably the most important progress in the use of these driers during the last decade is careful programming to obtain the fastest drying with a minimum of heat damage.

#### Moving-bed Drying

A modification of the belt drier is the fluidized bed where air flow from beneath is sufficient to lift particles of food and, at the same time, convey it toward the outlet. If air flows are too great channelling will occur, permitting most of the air to escape without performing its function. This type of drier is very efficient in the early stages of drying when high temperatures can be used but it may also be used as a finishing stage when bed depth is increased and temperature is lowered. A schematic diagram of a fluidized-bed drier is shown in Figure 1.

Two other examples of moving-bed driers, with high evaporative capacities, are the belttrough and rotary types. Both are throughbed driers in which the bed is moved mechanically. High drying temperatures can be used because of extensive cooling of the product due to evaporation, and air is seldom recirculated because it is frequently discharged near saturation. Most have carrying flights incorporated to turn the bed over in a particular way. Figure 2 shows a pilot-scale belt-trough drier which has a bed area only 4 ft by 2 ft but has an evaporative capacity up to 250 lb of water per hour. A rotary drier is depicted in Figure 3.

#### Freeze-drying

Freeze-drying has been the subject of intensive investigation in many laboratories over the last two decades. Most research has been directed toward shorter drying times and therefore a reduction in drying costs. This would permit extension of freeze-drying from high-cost raw materials, to which it is restricted at present, to a wider range of cheaper foods. Two significant advances have been made in the CSIRO Division of Food Research. One is the cyclic-pressure process and the other is cyclic pressure using a closed system containing helium.

In spite of their cost the use of freeze-dried foods is slowly increasing; many are mixed with other cheaper ingredients in dried soups, ready-to-serve meals, and coffee. Many freeze-dried products have good colour and flavour but probably their greatest advantage is their porous structure, which allows rapid rehydration.

#### Puff-drying

Another process, puff-drying, results in the production of a porous dried material. A prepared food is first dried to a moisture content of 30-40% by one of a number of drying procedures. The particles are then enclosed in a specially constructed 'gun' and heated using a gas flame on the exterior of the rotating barrel while superheated steam is applied internally to prevent scorching. Rapid release of pressure generated within the 'gun' causes water in the particles to vaporize producing a porous structure. The particles are then dried to 4-5% by conventional methods. The moisture content of the food entering the gun is usually critical if puffing is to be successful.

#### Microwave Drying

Potatoes and apples have been dried experimentally by using microwaves. Irregular drying usually occurs if attempts are made to dry foods starting from the fresh state. Charring may occur next to insufficiently dry sections. This problem is due mainly to unevenness in the flow of energy because of irregular shapes and density of the prepared food pieces. The process is more likely to be applicable to finish-drying because microwaves are preferentially absorbed by water. The only major applications at present are the finish-drying of potato crisps and bread rolls, when a uniform colour results.

#### Osmotic Drying

Fruits have been reduced to 50% of their initial weight by osmotic drying. Pieces are immersed in a concentrated syrup for eight hours at ambient temperatures for equilibrium to be attained between solids of the fruit and those of the syrup. This partial dehydration is completed by either air or vacuum drying although the latter is by far the better. Osmotic drying has a protective effect upon colour and flavour of the fully dried fruit and permits the production of a high-quality material with little or no sulphur dioxide. The cost of production is high, particularly if vacuum drying is used.

#### Azeotropic Drying

One of the most unusual methods of drying is called azeotropic drying. This consists of mixing or injecting a food with a solvent such as ethyl acetate. The azeotrope formed from the solvent and water of the food is boiled off under vacuum, say 100 mmHg at 25°C or 25 mmHg at  $-19^{\circ}$ C. The residual solvent is removed in a vacuum oven at 38°C. This method may be used for large pieces of food since the solvent penetration accelerates the rate of water diffusion. The latent heat of vaporization of ethyl acetate is only about 200 Btu/lb. The last traces of solvent are



difficult to remove and colour and flavour components may be removed by the solvent.

#### Bin Drying

Bin drying is an example of selecting the right drying conditions to suit a particular product. It is used to reduce moisture levels of particulate foods from 10-15% to 3-5%, a range in which drying rates are limited by slow diffusion of water. Temperatures of 100 to  $120^{\circ}$ F and air speeds of about 100 ft/min suit the nearly dry products because these conditions minimize the risk of heat damage at a stage when products are most susceptible to degradative chemical changes.

The intelligent use of bin drying increases plant capacity, permits handling flexibility, and results in significant economies. The process has been known for many years but its use has recently increased sharply.

Bins usually carry beds of material up to 5 ft in depth. They may be stationary with their own air and heat supply or they may be mobile and capable of being coupled to a ducted air system. Continuous bins use a slowly moving belt passing over an air grid.

During bin drying, which may take up to 36 hr, water contents are equalized as well as reduced. Air for the process is frequently dehumidified by condensation of water using refrigeration, or by removal using silica gel or sprays of lithium chloride.

Most of the preceding drying methods apply to solid subdivided foods. For liquids or foods which are homogenized, a different group of drying procedures are used.

#### Spray Drying

This procedure is used to dehydrate more food products than all others together. The liquid or slurry is dispersed in a stream of heated air and the dried particles are collected after separation from the air. Each product needs its own set of drying conditions such as size of atomized particles, type of air flow in the drying chamber, air temperature, separation, and collection method, but the basic principles have remained unchanged for many years.

Only one different drier of this type has been developed in recent years. It is known as the Birs drier. Droplets of liquid fall from the top of a 200-ft tower through a rising air flow whose inlet temperature is only 50°C. Air is dehumidified before heating. Although the process received considerable publicity initially it now appears that high capital and operating costs will prevent its widespread adoption.

#### Drum Drying

Drum driers have been used for many vears in the food industry. Initially they were the main milk-drying equipment but spray driers have gradually replaced them. Recently a wide range of foods have been dried on drums, one of the most important being potato. Up to five applicator rolls build up a layer of mashed cooked potato to a certain thickness on the single drum. Double drums are sometimes used to dry products such as apple, apricot, berries, and prunes. Due to their thermo-plasticity, foods containing large amounts of sugar are difficult to remove from drum driers; chilled air directed to a narrow strip just before the removal blade cools the thin sheet of food sufficiently to allow its ready removal.

Fibre retained in a food slurry often results in easier removal of the product from a drum drier than if the fibre is removed.

#### Pneumatic Driers

For certain liquid or puréed foods, pneumatic driers have been used. Air at temperatures up to 150°C is forced at high speed upwards through a Venturi throat. The food is metered into the throat, lifted by the hot air, retained until dry, and then carried into a cyclone separator.

#### Foam-mat Drying

One experimental food-drying process that has been developed to commercial size is foam-mat drying. Food is homogenized, using a foaming or stabilizing agent and sometimes in the presence of an inert gas. The stable foam is spread on a continuous belt in a tunnel 75 ft long, where it dries in 14–20 min. Powders with residual water levels of 2–3% result and they reconstitute readily due to their porous nature. Some of the products which have been dried by this method are banana, blackcurrant, grapefruit, orange, pineapple, raspberry, and tomato.

#### Diffusion Drying

An interesting method of drying reported recently is called diffusion drying. A liquid is spread on a belt with minute holes in it. Air is pushed through the holes and makes small capillaries in the liquid, drying it at the same time. The product dries from the base upwards and the resultant material is spongelike in structure. Inert gas may be used as the drying agent to reduce oxidative deterioration, and dehumidified air at low temperature is employed as the drying medium.

#### Aggregation

Small individual particles of dried food absorb water readily but a mass of powder is not easy to reconstitute, as penetration of water is blocked by swelling of the outer particles which form a barrier. By agglomerating particles, water uptake is improved greatly due to suction into the capillaries. This process, which is sometimes called 'instantizing', involves mixing the already dry powder in a warm and moist atmosphere. Aggregates are formed as water vapour is absorbed, and when they have reached the specified size they are re-dried in equipment such as a fluidized bed.

#### Reverse Osmosis

This procedure is a means of concentrating liquids such as fruit juices or whey. At present the degree of concentration is limited to about 30° Brix. As more suitable membrane support systems are developed higher concentrations may be achieved. Even now it is useful as a pre-drying process, particularly as it can remove large amounts of water at ambient temperatures while retaining a high proportion of the volatile flavour components. Concentrates may be finish-dried by spray drying, drum drying, or foam-mat drying.

#### **Intermediate Moisture Foods**

Finally, one interesting study relates to what have been called 'intermediate moisture' foods. Bacteria will not grow if the water activity\*  $(a_w)$  is below 0.9 and yeasts and moulds are inhibited below an  $a_w$  of 0.7. The foods previously discussed in this paper usually have been dried to water levels where the  $a_w$  is 0.1 or lower. The intermediate moisture food is one which is dried to an  $a_w$ of between 0.7 and 0.8, and then packaged with an antimycotic such as sorbate to suppress mould growth, e.g. the so-called 'soft, moist' pet foods. Wet and dry ingredients along with anti-mycotics are mixed to form a microbially stable mixture before packing. Material such as this avoids much of the heat damage, texture deterioration, and oxidative changes that are common to most dried foods.

#### Conclusion

The number of methods of water removal is probably not yet exhausted but it seems likely that many dried foods of the near future will be made by using one or more of the already known procedures. Even now, many of the driers used for foods have been 'borrowed' from other industries, such as chemical manufacture. These are selected firstly so that biochemical and biophysical characteristics of a food will be altered as little as possible, or alternatively so that changes will be made in these factors which may make them more acceptable than those of the original foodstuff.

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<sup>\*</sup> Water activity is defined as the ratio of the water vapour pressure in equilibrium with a food to the vapour pressure of water at the same temperature.

# **Protective Properties of Food Packaging Materials**

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This article is based on a paper presented by the author to the 12th Meat Industry Research Conference, July 1970, at Hamilton, New Zealand.

Flexible film materials currently available for the packaging of foods may be classified broadly into metallic foil, paper, regenerated cellulose, and a group made from organic polymers. Some of these, particularly the polymers, consist of a large number of individual types. In practice, these basic materials are seldom used alone, but more often in the form of coated and laminated structures, whereby the desirable properties of a number of individual materials may be combined into a single web.

There are many factors which determine the suitability of a material for the packaging of foods. These include cost, machine handling and sealing characteristics, general appearance, printability, resistance to mechanical and climatic hazards, freedom from toxicity, and protective properties.

This article deals with some of the protective properties of flexible films and film containers, including their gas and vapour permeabilities and their tainting characteristics, with particular reference to problems that have been investigated in the CSIRO Division of Food Research.

#### **Permeability Properties**

Meat products impose a variety of demands on the gas and vapour permeability properties of package materials. For instance, they require films that have some resistance to the permeation of water vapour; in the case of fresh and cured meats, excess loss of moisture should be avoided, whereas with dried meats the uptake of moisture from the storage atmosphere should be controlled. On the other hand, prepackaged fresh meats require films that are highly permeable to oxygen in order to maintain colour, but cured and dried meats require films having low oxygen permeabilities to avoid discoloration and rancidity.

There are two processes by which gases and vapours may pass through packaging films:

- A pore effect whereby the gas flows through small pores or pinholes in the material, and
- A 'solution-diffusion' process whereby the gas dissolves in one surface of the film, diffuses through, and evaporates from the other surface.

Aluminium foil in thicknesses of less than approximately 0.001 in. contains pores and may transmit gases by the first mechanism only; in the absence of pores it is impermeable. Both mechanisms occur in sufficiently thin plastic films, but most commercial films are pore-free and permeation occurs by the 'solution-diffusion' process.

Diffusion through pores is of importance in food packaging. In addition to metal foils and thin unsupported plastics, pores may also occur in thin coatings of plastic or wax on porous substrates such as paper and board, and in the heat seals of packages. The quantity of gas transmitted through a pore is influenced markedly by its dimensions and by the difference in either partial or total pressure of gas across the film surface. The influence of pores on the permeability of packages has been discussed by Becker (1963), who pointed out that a mathematical treatment of the process is impractical because of the difficulty in defining pore dimensions.

The 'solution-diffusion' mechanism of gas permeation has been fully developed mathematically. According to Barrer (1951), true permeability, P, of a gas in a homogeneous polymer film may be expressed by the equation

$$P = qL/At\Delta p, \tag{1}$$

where q is the quantity of gas passing through the film of thickness L and area A in time t under a partial pressure difference  $\Delta p$ . He further showed that under ideal conditions

$$P = DS, (2)$$

where D is the diffusion constant of gas in the film and S is the solubility coefficient. The diffusion process may be envisaged as the movement of gas molecules from the high concentration to the low concentration side of the film as a result of random molecular movements. The process, therefore, is not dependent on the presence of actual pores passing right through the film, but on the continual formation and disappearance between polymer chains of microcavities into which the gas molecules move under the influence of the difference in gas concentration at the two film surfaces.

Although the permeation theory outlined applies to a large number of gas-polymer systems, deviations from ideal behaviour do occur. Hennessy, Mead, and Stening (1966) have discussed from a practical point of view the various factors that influence gas and vapour permeability, and outlined some methods for the measurement of permeability. A more fundamental treatise has been published by TAPPI (1962).

#### Effect of Pressure

When corrected to unit pressure difference, the permeability of polymer films to permanent gases is independent of the pressure at which the measurements are made, but deviations do occur with some vapours. Davis (1965) has shown that the water vapour permeability of nitrocellulose-coated cellulose, and to a lesser extent that of a laminate of this material with polyethylene, was influenced by the relative humidity (R.H.) level at which the measurements were made. The coated cellulose film, for instance, gave values of 0.08 and 0.30 g m<sup>-2</sup> day<sup>-1</sup> Torr<sup>-1</sup> at 25°C when tested at 20% and 80% R.H. respectively. In other words, it was four times more permeable at 80% R.H. than at 20% R.H.

In general, such effects are shown by hydrophilic materials, such as regenerated cellulose, glassine, and some of the polyamide films, but not with hydrophobic films such as the polyolefins, polyvinyl chlorides, and polystyrene.

The phenomenon is attributed to a pressure-dependent solubility coefficient—i.e. failure to obey Henry's law—and, in cases where the vapour is highly soluble in the film material, to a plasticizing effect which leads to an increase in the diffusion coefficient with increasing pressure.

Another departure from ideal permeation behaviour of importance in food packaging concerns the effect of water vapour on the gas permeability of films. Generally, the permeation of a specific permanent gas is not influenced by the presence of other permanent gases, but it may be markedly affected by the presence of highly soluble vapours that function as plasticizers for the film material. Regenerated cellulose films, for instance, are excellent barriers to dry gases and, until a few years ago, it was common practice to determine their permeabilities using dry gases. Work since that time has shown that the gas permeability of these films is markedly influenced by the R.H. of the gas (Davis 1964). For instance, nitrocellulose-coated cellulose films and laminates of these films to polyethylene are 1000 times more permeable to oxygen at 92% R.H. than at 0% R.H. Similar materials coated with polyvinylidene chloride (PVDC) showed a 15-fold increase in oxygen permeability over the same R.H. range. The difference in the effects of the two types of coating on cellulose films has been attributed to an effect of the PVDC coating whereby the base cellulose is prevented from swelling in the presence of moisture (Notley 1963).

#### Effect of Tèmperature

Another variable that may affect permeability is temperature. With most polymerpenetrant systems, both the solubility and diffusion coefficients, and hence the permeability, obey the Arrhenius relationship.

Thus

$$P = P_0 \exp(-E_p/RT), \qquad (3)$$

where  $P_0$  is a temperature-independent constant,  $E_p$  is the activation energy for the permeation process, R is the gas constant, and T is the absolute temperature.  $E_p$  is the sum of the activation energy for the diffusion process,  $E_d$ , and the heat of solution,  $\Delta H$ .  $E_d$  is always positive, and the diffusion coefficient increases with increasing temperature.  $\Delta H$  is small and positive for the permanent gases, but negative for easily condensable vapours. Hence solubility increases slightly with increasing temperature for permanent gases, but decreases for vapours. The permeability of a specific polymer-penetrant system, therefore, may increase or decrease with increases in temperature, depending upon the relative effect of temperature on the solubility and diffusion coefficients of the system. For this reason, permeability values of different types of film determined at one specific temperature may not be in the same relative order at other temperatures.

As suggested by equation (3), the effect of temperature on permeability may be studied conveniently from a plot of log permeability versus the reciprocal of the absolute temperature. In many cases such a plot gives a straight line which enables permeability values at temperatures other than those studied to be estimated with reasonable accuracy.

Before 1970 there was a notable lack of reliable data on the water vapour permeability of films at temperatures below 0°C, which are necessary to meet the requirements of the frozen foods industry. Moreover, the evidence suggested that the extrapolation of water vapour permeability data, determined at nearambient temperatures, to below 0°C could lead to serious errors. Karel. Proctor, and Wiseman (1959) showed that the water vapour permeabilities of both polyethylene and Saran films, determined at constant R.H. and corrected to unit vapour pressure difference, decreased with decreasing temperature from 57°C to 20°C, but polyethylene was more permeable at 2°C than at 20°C. The data of Kunis (1964) suggest that both the above films are more permeable to water vapour at  $-20^{\circ}$ C than at 20°C. His value for polyethylene at  $-20^{\circ}$ C is in good agreement with that reported by Simerl (1953) at  $-18^{\circ}$ C. However, all these reported values were determined by gravimetric techniques. Recently Becker and Heiss (1970) studied the water vapour permeability of a range of materials for temperatures from 50°C to -20°C using a sensitive electrolytic moisture meter. They showed that the log P versus 1/T relation is essentially linear for polyethylene, polyvinyl chloride, Cryovac SA739, and a polyethylene/ paper laminate, but non-linear for laminates of polyester/polyethylene, polyamide/polyethylene, and PVDC/paper.

#### Effect of Pinholes

Minute pores or pinholes that completely penetrate packaging materials lead to an increase in gas and vapour permeability, a rapid loss of vacuum in vacuum-packs, and an increase in the risk of microbial contamination of packaged foods. Pinholes that penetrate individual layers of coated and laminated webs are less serious, but they may still significantly affect the protective properties of materials.

Table 1
Oxygen Permeability of PVDC Film and PVDC-coated
Papers
$\mathbf{D}_{1} = 1.117 + 1.000 \text{ (GTD)} = -2.11.760 \text{ Tr} = -1.(25\%)$

Permeability	in cc	(SIP)	m-" aa	iy - 70	J 10rr	- (25°C	
		65 °⁄	6 R.H.)	)			

Type of Paper	10 <sup>3</sup> × Coating Thickness (in.)	Oxygen Permeability
Plain PVDC film	1.00	5.0
Opaque superglazed	0.39	460
	0.58	390
	0.58	4.6
	0.70	310
Glazed imitation		
parchment	0.58	8.2
-	0.58	110
	0.70	79

We first encountered the importance of pinholes in barrier coatings during an investigation of the oxygen permeability properties of papers coated with PVDC. Table 1 shows some typical results observed on two types of coated papers. In the absence of pinholes, the oxygen permeability of unsupported PVDC film is low compared with other plastics, and it should be inversely proportional to thickness. The values observed on the coated papers, however, show no relation to film thickness. Although pinholes were suspected to be causing the anomalies, attempts to detect their presence using dye solutions, such as methylene blue in ethyl alcohol, as penetrants were not successful. Subsequently a more sensitive test, described in detail by Davis (1969), satisfactorily demonstrated that specimens of the coated paper having oxygen permeabilities of approximately 15 cc STP m<sup>-2</sup> day<sup>-1</sup> 760 Torr<sup>-1</sup> or less were free of pinholes, whereas those which gave higher values contained one or more pinholes.

The test is based on the diffusion of ammonia under a pressure difference through the pinholes, and its subsequent detection as spots on a paper coated with an ammoniasensitive reagent. The test has also been applied successfully to the detection of pinholes in wax coatings on papers, both before and after creasing. Although the test is not suitable for the detection of pinholes in coatings on non-porous substrates, such as polymer or regenerated cellulose films, it may be used to determine the incidence and precise location of pores that completely penetrate these materials.

and oxygen permeabilities have been described by Davis (1965) and Davis and Burns (1969) respectively. Table 2 shows a comparison of the water vapour permeabilities determined by the test-cell and package methods on a range of films. The test packages were pouches fabricated in the laboratory by fin sealing. The two methods gave similar values with polyethylene, but with nitrocellulosecoated cellulose the results for packages were higher than those determined by the cell method. This difference may be attributed to heat and mechanical damage to the nitrocellulose coating during construction of the packages. Packages made from some types of laminates are also known to have higher

Table 2
Comparison of Water Vapour Permeabilities Determined by Test-cell and Package Methods

Permeability in g m<sup>-2</sup> day<sup>-1</sup>

		Water Vapour Permeability		
Material	Test Condition	Test-cell Method	Package Method	
Polythene (0.001 in.)	25°C, 65 % R.H.	$4 \cdot 0$	3.3	
Nitrocellulose-coated regenerated cellulose	25°C, 65% R.H.	$1 \cdot 1$	3.6	
PVDC (25 g/m <sup>2</sup> )/paper/polyethylene ( $0.001$ in.)	38°C, 90% R.H.	1.5*	3.9*	
Paper/polyethylene (0.001 in.)/PVDC (17 g/m <sup>2</sup> )	38°C, 90% R.H.	2.1†	2.6†	

\* Polyethylene side facing desiccant.

† PVDC-coated side facing desiccant.

#### Permeability of Packages

Data reported in the literature on the permeability of packaging films are usually determined on small disks of the test material by one of the test-cell techniques. Such tests do not take into account a number of variables associated with the fabrication of packages, such as the effects of heat sealing, creasing, and general machine damage, each of which may influence the performance of the fabricated package. Most standard methods for the determination of water vapour permeability specify procedures for creasing test specimens, and the difference between the values observed on creased and uncreased specimens is used as a guide to the fabrication properties of the material.

The safest approach, however, is to carry out the measurements on the fabricated package, and the methods we use for water vapour permeabilities than indicated by test-cell results. For instance, the results in Table 2 show that fin-sealed packages made from a PVDC/paper/polyethylene laminate are more permeable to water vapour than might be expected from the test-cell results. In this case, water vapour is able to diffuse into the paper at the edges of the seal, then permeate through the polyethylene layer, thus by-passing the less permeable PVDC layer. With the second structure, where the less permeable PVDC layer was inside the package, the package and test-cell values were similar.

One interesting application of the package method for determining oxygen permeabilities was encountered recently. This investigation was designed to determine the permeability of a range of packages for processed meats in which one web of material was thermoformed into the shape of a tray, then sealed with a flat web of a different material. In this type of package the thermoforming operation introduces considerable variations in thickness and a surface area that is difficult to define. These effects, coupled with the presence of two different types of material, made it impractical to calculate the package permeability from test-cell values determined on flat specimens of the materials. Using the package method, however, it was possible to determine accurately the amounts of oxygen permeating into the packages.

#### **Tainting Properties**

In addition to preventing the uptake of undesirable odours and the loss of desirable odours by permeation, compounds present in package materials should not migrate and contaminate foods. Contamination may occur by chemical interaction between the product and the container, such as corrosion of metal, or solution and absorption processes in non-metallic materials. When the product and package material are in direct contact, both volatile and non-volatile compounds may migrate into the product, but volatile compounds may also be picked up from the container headspace even when there is no direct contact.

The majority of taints in packaged foods are caused by absorption of volatile compounds released from the package material. Harvey (1963) has published a useful survey of the problem of odours in the packaging of foods.

Several empirical procedures are available for testing the tainting properties of materials. One useful preliminary method for determining odour properties involves placing the sample, torn into small pieces and crumpled, into odour-free glass jars fitted with glass stoppers, and smelling the jar atmospheres after a 24-hour storage period. A few drops of water should be added to the jars beforehand since the odour of some materials is more pronounced at high humidity. Materials which show evidence of odour by this method should be treated with caution and subjected to taste tests with the food to be packaged, or with other suitable test foods.

Where the food has a strong natural flavour, tainting tests have the disadvantage that considerable contamination may have occurred but cannot be detected. To overcome this difficulty, foods that have mild natural flavours, yet are representative of aqueous and fatty foods, are often used as test products. Such foods include water, butter, milk chocolate, dried milk, and hydrogenated coconut oil. The test product may be packed and stored before tasting in the fabricated packages, but a more sensitive test is to carry out taste tests on small samples of the food which have been stored in the atmosphere of glass jars containing crumpled pieces of the package material.

We have investigated a number of outbreaks of tainting in packaged foods using these empirical techniques. In two of these cases, the foods were packed in polystyrene trays and overwrapped with a PVDC-coated cellulose film that is known to be highly impermeable to organic odours. The odour of the objectionable compound was found to resemble that of styrene monomer. Evidently, traces of the monomer had been released from the tray material and had accumulated in the atmosphere within the wrap in amounts sufficient to impart an objectionable taint to the food. Similar circumstances were found to be the cause of an off-flavour in frozen foods bulk packaged in refrigerated shipping containers insulated with a polyester resin cross-linked with styrene. Residual styrene monomer had accumulated within the sealed container and had been absorbed by the food.

Tainting problems arising from packaging materials are also amenable to more fundamental studies using modern instrumental procedures such as gas chromatography, mass spectroscopy, and ultraviolet and infrared spectrometry. One such problem investigated recently concerned a 'sweet-buttery' odour evolved from aluminium foil that had been printed and lacquered with nitrocellulose. A concentrate of the foil odour was collected and examined with a sensitive gas chromatograph. The chromatogram revealed the presence of 88 peaks, each of which represented one or possibly more chemical compounds. Chromatograms were then obtained from concentrates of the acetone, methylethyl ketone, and ethyl alcohol solvents used in the formulation, and these showed 65, 70, and 9 peaks respectively. These solvent peaks were obviously caused by impurities in the solvents. Moreover, the retention times of some of the solvent peaks were close to those observed on the original foil odour which suggested that the foil odour was due to the presence in the commercial solvents of trace impurities that were not removed during stoving of the lacquer film.

Steps taken by the manufacturer to improve the efficiency of the stoving operation and to use purer grades of solvent resulted in a decrease of the odour to an acceptable level.

The foil investigations demonstrate the complex nature of some odour problems. The original foil odour was probably a mixture of two or more individual compounds, each at a specific concentration. It would obviously be a mammoth task to identify positively the compounds responsible for the chromatographic peaks detected, to estimate their concentrations quantitatively, then to determine which combination of compounds was responsible for the 'sweet-buttery'odour.

In concluding, I should like to emphasize that the quality of many foods depends markedly on the protective properties of the containers in which they are packaged. Food manufacturers, therefore, should ensure that all package materials are thoroughly evaluated before the pack is marketed.

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### News from the Division

FRL, Food Research Laboratory; MRL, Meat Research Laboratory; DRL, Dairy Research Laboratory; PPU, Plant Physiology Unit

#### **New Appointments**

On July 6, 1971, Ministerial approval was given for the appointment of Dr B. S. Harrap as Officer-in-Charge of the Dairy Research Laboratory and Assistant Chief of the Division of Food Research. Dr Harrap was formerly Leader of the Leather Research Section of the CSIRO Division of Protein Chemistry. In that capacity he established close contacts with industry and his appreciation of industry problems and of the benefits to be gained through the application of science and advanced technology should result in further advances in Australia's dairy manufacturing processes.



Dr B. S. Harrap.

After graduating B.Sc. from the University of Melbourne in 1945 and Ph.D. from the same university in 1949, Dr Harrap joined the CSIRO Division of Industrial Chemistry to work on the adsorption of liquids by activated carbon.

In 1950 he was awarded a Zinc Corporation Research Scholarship and went to Britain where he gained a further Ph.D. at the University of Cambridge for his work on interactions between detergents and proteins.

He returned to CSIRO in 1952 and spent the next fourteen years with the Division of Protein Chemistry studying the structure of soluble wool proteins and working on a method of dyeing wool at low temperatures using formic acid as a dye solvent. During this period he spent 12 months at Harvard University carrying out research on muscle protein.

In 1966 Dr Harrap was appointed Leader of the Division of Protein Chemistry's Leather Research Section. Under his leadership the Section made a number of important practical contributions to the Australian leather industry. At the same time the Section carried out a good deal of research of a more fundamental nature on the interactions between tanning agents and collagen, the main protein constituent of hides and skins.

Dr Harrap will be overseas for about six months in the second half of 1971 and during his absence Mr J. Czulak will continue as Acting Officer-in-Charge of DRL.

Dr A. Shneyour has been appointed to the Division's Plant Physiology Unit to study the properties of membrane proteins from the chloroplasts and mitochondria of chillsensitive plants.

Miss Anne Fisher joined the Meat Research Laboratory on May 17, 1971, to work on the taste evaluation of meat and meat products and the relationship of this evaluation with various objective assessments of meat quality.

#### Retirement

Dr A. Howard of the MRL retired recently after almost forty years with CSIRO.

Dr Howard graduated B.Sc. in chemistry in 1926 and M.Sc. in 1928 from the University of Melbourne. In 1929 he accompanied Sir Douglas Mawson to the Antarctic as a hydrologist with the British Australian New Zealand Antarctic Research Expedition.

He joined CSIRO on his return to Australia in 1931, working first at the Irrigation Research Laboratory at Griffith. During the war he transferred to the Division of Food Preservation and Transport to work on the preservation of meat and vegetables by dehydration. Later he moved to Brisbane where his work on the complex interrelation of chemistry and psychology in interpreting flavour differences led to the award of a Ph.D. degree in psychology in 1968.

Following the retirement of Dr Howard and Dr G. Kaess (*CSIRO Fd Res. Q*, **31**, 29), it was decided to combine the Meat Quality and Processing and Utilization Sections of MRL; the expanded section is known as the Meat Science and Technology Section (Leader Mr J. J. Macfarlane).

#### Visiting Workers

Towards the end of June, Dr Norman E. Looney, of the Summerland, B.C., Research Station of the Canada Department of Agriculture, joined the Plant Physiology group at Ryde, for a period of 12 months. Dr Looney will be working in collaboration with Dr W. B. McGlasson on the action of Alar\* in delaying the ripening of fruit.

Professor F. D. Carroll of the University of California's Department of Animal Science is spending approximately four months of his sabbatical leave at MRL.

#### General

In 1970 the Standards Association formed a committee to draw up methods for the examination of eggs and egg products; Mr D. F. Ohye and Mr F. S. Shenstone of FRL were nominated members. Subcommittees were then appointed: one for chemical methods of examination, chaired by Mr Shenstone and including Dr J. R. Vickery (former Chief of the Division), the other for microbiological methods of examination, Dr J. H. B. Christian (Associate Chief) being a committee member.

The Australian Institute of Food Science & Technology Annual Convention, held in Sydney from May 31 to June 7, attracted a considerable number of participants from all three of the Division's laboratories. At the Annual General Meeting of the Institute, Mr J. F. Kefford (Assistant Chief) was elected Federal President of A.I.F.S.T., thus creating a 'triumvirate' in the Division: Mr M. V. Tracey (Chief) is currently President of the Australian Biochemical Society, while Dr J. H. B. Christian (Associate Chief) is President

\* Uniroyal Chemical Corp.: succinic acid-2,2-dimethylhydrazide. of the Australian Society for Microbiology. In addition, Dr Christian was elected to the 22-member International Commission on Microbiological Specifications for Foods. The Commission is concerned with the microbiological quality of foods in international trade. Dr Christian attended a meeting of the I.C.M.S.F. held in Yugoslavia in May.

A two-day course on the use of flame sterilization techniques by the food industry will be held on November 18 and 19, 1971, at FRL, North Ryde, under the joint auspices of the Food Engineering Group of the N.S.W. Branch of the Institute of Food Science and Technology and the Division of Food Research. Lectures and practical demonstrations will be given to technical personnel from the food industry. Further particulars may be obtained from the Technical Secretary of the Division.

The Australian Institute of Food Science and Technology elected to Fellowship the following members of the Division: Miss Barbara Keogh (DRL), Mr E. G. Davis (FRL), Mr D. McG. McBean (FRL), Dr K. E. Murray (FRL), and Mr D. J. Casimir (FRL).

Mr L. E. Brownlie, Leader of the MRL's Industry Section, visited meat research centres in the U.S.A. and attended meetings of the American Meat Institute Foundation, the American Meat Science Research Conference, Food Research Institute, and American Society for Microbiology between March and May 1971.

Dr C. J. Brady (PPU) visited several research centres in the U.S.A., Britain, Europe, Israel, and Malaysia between March 27 and July 3, 1971.

Mrs W. Szulmayer (FRL) made a private visit to the U.S.A., Britain, and Europe and took the opportunity to attend the International Conference of the Solar Energy Society, N.A.S.A.

During a private visit to Europe in June, Dr R. M. Smillie attended the International Congress of Photosynthetic Research at Stresa in Italy where he presented two papers.

Mr D. G. James of the Tasmanian Regional Laboratory accepted an invitation to spend twelve months in Denmark at the Ministry of Fisheries Technological Laboratory at Lyngby, participating in a course organized under the auspices of the United Nations (F.A.O.). Miss E. A. Chapman (PPU) is spending approximately six months in the Department of Environmental Biology, Research School of Biological Sciences, A.N.U., Canberra.

Dr A. R. Johnson represented CSIRO at meetings of C.E.M.A. and the Chicken Meat Advisory Research Committee.

Mr M. V. Tracey visited Tokyo in May for discussions with Presidents of the Indian and Japanese Biochemical Societies.

Mr E. G. Hall (FRL) and Professor I. L. Eaks, visiting worker from the University of California, Riverside, gave papers at an Extension School on Post-harvest Treatment of Citrus Fruits, held at the Citrus Wastage Research Laboratory, Gosford, in April 1971 under the joint auspices of the New South Wales Department of Agriculture and CSIRO.

#### Specialist Course on Instrumental Techniques

The course referred to in previous issues was held at FRL from July 19 to 23, 1971, and was attended by 33 participants from industry

and government food establishments. Copies of the course textbook are available from the Division's Technical Secretary at \$5 each.

#### International Congress on Canning

The Comité International Permanent de la Conserve will hold the 6th International Congress on Canning in Paris on November 13–17, 1972. The Congress will include discussions on all aspects of pollution and on the pre-treatment of raw materials for the canning industry.

Interal 72 (Biennale Internationale, 'Alimentation et Techniques'), which groups together seven exhibitions including Salon International de l'Alimentation, Salon International de l'Equipement des Industries de l'Alimentation, and Salon de l'Emballage, will take place at the same time, so those attending the Congress will also have the opportunity to visit outstanding exhibitions of foods, food machinery, and packaging.

Additional information about the Congress may be obtained from M. Henri Cheftel, J. J. Carnaud & Forges de Basse-Indre, Boîte Postale 105, Billancourt, France.

### Selected Publications of the Division

#### From the Dairy Research Laboratory

Copies of most of these papers are available from the Librarian, CSIRO Division of Food Research, Dairy Research Laboratory, Box 20, P.O., Highett, Vic. 3190. (Telephone 95 0333.)

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- LLOYD, G. T. (1971).—New developments in starter technology. *Dairy Sci. Abstr.* **33**, 411.
- ZADOW, J. G. (1971).—Some theoretical aspects of casein washing. Pts. 1 and 2. Aust. J. Dairy Technol. 26, 9–17.

#### From the Food Research Laboratory

Copies of most of these papers are available from the Librarian, CSIRO Division of Food Research, Food Research Laboratory, Box 52, P.O., North Ryde, N.S.W. 2113. (Telephone 888 1333.) Those marked \* are no longer available.

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- JAMES, D. G. (1970).—Shark tag discoveries can help you. Prof. Fish. Ass. Tas. Mag. 1, 166–7.\*
- JAMES, D. G., and OLLEY, JUNE (1971).—Spoilage of shark. Aust. Fish. 30(4), 11–13.
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- KEFFORD, J. F., and CHANDLER, B. V. (1970).—The chemical constituents of citrus fruits. Adv. Fd Res., Suppl. No. 2. 246 pp.\*
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- MIDDLEHURST, J., and FISHER, L. R. (1971).—Polywater on silica-free substrates. *Nature* 230, 575.
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- OHYE, D. (1971).—Tolerance of bacteria to high concentrations of sodium chloride and glycerol in the growth medium. *Appl. Microbiol.* **21**, 363–4.
- OLLEY, JUNE (1970).—Future trends in protein production. Proc. 13th ann. Conf. Aust. Ass. agric. Fac. p. 77.\*
- PONTING, J. D.,<sup>†</sup> and McBEAN, D. M. (1970).— Temperature and dipping treatment affects drying rates and drying times of grapes, prunes and other waxy fruits. *Food Technol.* 24, 1403–6.
- † Not a member of the Division.

- RILEY, T. J. (1969).—Gas analysis with the Orsat. Pap. Extension School on Controlled Atmosphere (C.A.) Storage of Apples and Pears held in conjunction with N.S.W. Dep. Agric., Orange, N.S.W. pp. 52–8.\*
- TRACEY, M. V. (1970).—Leaf protein: a new source of food protein for man. *Etruscan* **19**(3), 5–8.\*
- VENDRELL, M. (1970).—Relationship between internal distribution of exogenous auxins and accelerated ripening of banana fruit. Aust. J. biol. Sci. 23, 1133–42.
- VICKERY, J. R. (1970).—Food preservation present and future. *Aust. Refrig. Air Condit. Heat.* 24(3A), 65–6.\*
- VICKERY, J. R. (1970).—Trends in the Australian meat industry. Fd Technol. Aust. 22, 416–17, 419.\*
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- WILLS, R. B. H., and MCGLASSON, W. B. (1971).— Effect of storage temperature on apple volatiles associated with low temperature breakdown. J. hort. Sci. 46, 115–20.

#### From the Meat Research Laboratory

Copies of most of these papers are available from the Librarian, CSIRO Division of Food Research, Meat Research Laboratory, Box 12, P.O., Cannon Hill, Qld. 4170. (Telephone 95 2122.)

- BOUTON, P. E., HARRIS, P. V., and SHORTHOSE, W. R. (1971).—Effect of ultimate pH upon the waterholding capacity and tenderness of mutton. J. Fd Sci. 36, 435–9.
- KAESS, G., and WEIDEMANN, J. F. (1971).—Extending storage life of chilled mutton by continuous irradiation with ultraviolet light. *Fd Technol. Aust.* 23, 62–6.
- LEDWARD, D. A. (1971).—Metmyoglobin formation in beef muscles as influenced by water content and anatomical location. J. Fd Sci. 36, 138–40.
- LEDWARD, D. A., and SHORTHOSE, W. R. (1971).— Haem pigment concentration of lamb as influenced by age and sex. *Anim. Prod.* **13**, 193–5.
- MARSHALL, BETTY J., and SCOTT, W. J. (1970).—The effects of some solutes on preservation of dried bacteria during storage *in vacuo*. Proc. int. Conf. Culture Collections, Tokyo, 1968. pp. 363–8.
- NEWBOLD, R. P., and SCOPES, R. K. (1971).—Postmortem glycolysis in ox skeletal muscle. Effects of mincing and of dilution with or without addition of orthophosphate. J. Fd Sci. 36, 209–14.
- NEWBOLD, R. P., and SCOPES, R. K. (1971).—Postmortem glycolysis in ox skeletal muscle. Effect of adding nicotinamide-adenine dinucleotide to diluted mince preparations. J. Fd Sci. 36, 215–18.