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Vacuolenvorming bij het verstuivingsdrogen

J. G. P. Verhey

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Proefschrift
ter verkrijging van de graad van
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Abstract

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Experiments with a pilot spray drier showed that vacuoles in spray-powder particles originate from air bubbles. These are dispersed in the liquid during spraying, before actual atomization. During drying, the air bubbles expand as a result of gradual solidification of the droplet surface ('case hardening') before drying is complete. The vacuole volume is governed by the degree of air incorporation (related to type and design of atomizer and properties of the feed liquid) and the bubble expansion (related, for instance, to inlet air temperature).

Vacuoles do not develop as a result of spontaneous boiling phenomena. Vacuole-free powders can be produced by replacing the air in the atomizer by steam.

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Stellingen

1

In de gebruikelijke vloeistofverstuivers wordt verneveling voorafgegaan door luchtinslag.

Dit proefschrift.

2

Vacuolenvorming bij het verstuivingsdrogen is een bijverschijnsel van de verstuiving; tijdens het drogen worden geen nieuwe vacuolen meer gevormd.

Dit proefschrift.

3

Bij vol melkpoeder is het verwijderen van een belangrijke hoeveelheid zuurstof door een herhaalde gasbehandeling mogelijk dankzij de aanwezigheid van vet.

Dit proefschrift.

4

De aanname van moleculaire diffusie bij het beschrijven van de massatransporten in drogende druppeltjes voert tot resultaten die ten dele in strijd zijn met experimentele gegevens.

H. A. C. Thijssen & W. H. Rulkens, De Ingenieur 80 (1968) 47.
J. v. d. Lijn, W. H. Rulkens & P. J. A. M. Kerkhof, Symposium on heat and mass transfer, F3, Wageningen 1972.

5

De wijze waarop Berlin en Pallansch de werkelijke dichtheid van deeltjes meten is onjuist.

E. Berlin & M. J. Pallansch, J. Dairy Sci. 46 (1963) 780.

6

Bij het bestuderen van 'vrij vet' in melkpoeder mogen de op het drogen volgende mechanische invloeden zeker niet worden vergeten.

T. J. Buma, proefschrift, Wageningen 1971.

7

Voor het beschrijven van de oproming in gecondenseerde melk dienen viscositeitsgegevens te worden gebruikt, die verkregen zijn bij extreem lage snelheidsgradiënten.

R. B. Macy & H. H. Sommer, J. Dairy Sci. 37 (1954) 60.

8

Het opstellen van een nomogram voor het aflezen van de viscositeit van gecondenseerde melk heeft weinig zin als geen rekening gehouden wordt met de eerdere verhitting van de melk en met andere parameters.

F. Fernandez-Martin, J. Dairy Res. 39 (1972) 75.

9

De hittestabiliteit van koffiemelk wordt vaak in verband gebracht met de pH vóór of ná het steriliseren, hoewel de pH tijdens de sterilisatie veel wezenlijker is.

D. Rose & H. Tessier, J. Dairy Sci. 42 (1959) 969.

10

De eigenschappen en toepassingsmogelijkheden van geheel of grotendeels door wei-eiwit gestabiliseerde vet-emulsies verdienen grote aandacht.

11

Produkten als waspoeder, koffiepoeder en veevoeder worden soms zo volumineus gemaakt, dat men wel zou kunnen spreken van letterlijke windhandel.

12

Onze samenleving biedt ruimte voor massale misleiding door reclame. De voorbeelden hiervan variëren van lachwekkend (tandpasta) tot zeer verontrustend (onverzadigd vet, zoete snacks).

13

Er is een nieuw zuinigheidsbegrip nodig als antwoord op de huidige consumptiementaliteit.

Proefschrift van ir. J. G. P. Verhey
Wageningen, 11 mei 1973

Curriculum vitae

In 1956 behaalde de auteur het diploma HBS–B aan het Ludgercollege te Doetichem waarna hij ging studeren aan de Landbouwhogeschool te Wageningen. Hier koos hij de studierichting Zuivelbereiding en Melkkunde. Na het kandidaatsexamen vervulde hij de militaire dienstplicht en in 1964 volgde het ingenieursexamen. Een jaar later behaalde hij aan de University of Wisconsin (Verenigde Staten) de graad van Master of Science in Dairy and Food Industries. Vervolgens was hij werkzaam als wetenschappelijk medewerker op het Laboratorium voor Zuiveltechnologie en Melkkunde van de Landbouwhogeschool. In januari 1973 werd hij hoofd van het Coberco Research Laboratorium te Deventer.

Deze publikatie is een samenvatting van een onderzoek dat uitvoerig wordt behandeld in de volgende tijdschriftartikelen:

I J. G. P. Verhey & W. L. Lammers: A method for the determination of the residual gas volume in dried milk products.
Neth. Milk Dairy J. 24 (1970): 96–105.

II J. G. P. Verhey: Air penetration into milk powder.
Neth. Milk Dairy J. 25 (1971): 246–262.

III J. G. P. Verhey: Vacuole formation in spray powder particles. 1. Air incorporation and bubble expansion.
Neth. Milk Dairy J. 26 (1972): 186–202.

IV J. G. P. Verhey: Vacuole formation in spray powder particles. 2. Location and prevention of air incorporation.
Neth. Milk Dairy J. 26 (1972): 203–224.

V J. G. P. Verhey: Vacuole formation in spray powder particles. 3. Atomization and droplet drying.
Neth. Milk Dairy J. 27 (1973): 3–18.

VI J. G. P. Verhey & W. L. Lammers: A method for measuring the density distribution among spray powder particles.
Neth. Milk Dairy J. 27 (1973): 19–29.

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Overdrukken/Reprints

1 Inleiding

Dit promotieonderzoek werd verricht van 1966 tot 1972 op de afdeling Zuivelbereiding en Melkkunde van de Landbouwhogeschool (nu sectie Zuiveltechnologie van de vakgroep Levensmiddelentechnologie). Voor de keuze van het onderwerp waren verschillende aanleidingen.

Het was bekend, dat in poederdeeltjes, bereid door het verstuivingsdrogen van vloeistoffen zoals melk, vrijwel altijd holle ruimten voorkomen (vacuolen genaamd). De gevolgen van dit verschijnsel zijn doorgaans nadelig. Zo vergroten de vacuolen het soortelijk volume van een poeder en bemoeilijken ze het verpakken van het produkt in een zuurstofvrije atmosfeer. Bovendien was uit praktijkervaring bekend, dat bij het instantizeren (snel oplosbaar maken) van verstuivingspoeder een laag vacuolenvolume gewenst is.

Het was niet bekend, hoe vacuolen ontstaan, ook al vermeldde de literatuur enkele ervaringsfeiten zoals de invloed van het type verstuiver (hogedrukverstuiving levert soortelijk zwaardere poeders dan centrifugaalverstuiving), van de aard van de uitgangsvloeistof (vet- en watergehalte van melk) en de procesomstandigheden (o.a. groter vacuolenvolume bij hogere droogluchttemperatuur). Deze kennis was ontoereikend om de vacuolenvorming naar wens te kunnen beïnvloeden. Naast deze praktische informatie waren er ook nog gegevens, afkomstig van theoretische berekeningen en modelproeven. Het is echter uiterst moeilijk om langs deze weg het proces dicht te benaderen en de vorming van vacuolen kan daarbij onvoldoende worden bestudeerd.

Besloten werd dan ook tot een zo fundamenteel mogelijke experimentele aanpak, gebruik makend van de op het laboratorium aanwezige kleine verstuivingsdroger, die daarvoor constructief gewijzigd werd.

2 Methoden

Als grondstof voor het verstuivingsdrogen werd meestal ondermelk gebruikt, hoewel ook andere melkprodukten werden gedroogd alsook koffieextract, ei, zeep. In de verticale droogtoren (die oorspronkelijk alleen van centrifugaalverstuiving was voorzien) werden ook pneumatische en drukverstuivers toegepast. Allerlei procesomstandigheden werden in velerlei combinaties gevarieerd.

Een uiterst belangrijk analytische techniek was de mikroskopie, waaraan vooral vele kwalitatieve gegevens werden ontleend. Ook andere reeds bekende analysemethoden werden toegepast, o.a. voor het bepalen van het volume van de vacuolen per 100 g poeder.

Verschillende nieuwe methoden waren echter nodig. Eén daarvan was van doorslaggevend belang voor de verdere ontwikkeling van het onderzoek, en wel de bepaling van de hoeveelheid lucht die aanwezig was per 100 g poeder. Hiertoe werd een monster van het poeder in heet water opgelost, waarna in daartoe ontwikkelde apparatuur het volume en het zuurstofgehalte van de vrijgekomen lucht werd gemeten. Een andere nieuwe methode was het bepalen van de hoeveelheid koolzuur, die aanwezig was in poeders welke bereid waren in aanwezigheid van dit gas in de verstuiver. Van de overige nieuwe methoden vermeld ik nog de toepassing van densiteitsgradiënten voor de bestudering van de dichtheidsverschillen tussen individuele deeltjes.

Het onderzoek culmineerde in een wijziging van het proces van verstuivingsdrogen waardoor de bereiding van vacuolenvrije poeders mogelijk werd. Dit zal in het volgende hoofdstuk behandeld worden.

3 Resultaten en discussie

3.1 Het restgasvolume (artikelen I en II)

Microscopisch lijken vacuolen op luchtbellen. Laat men de holle poederdeeltjes in water oplossen, dan blijven er ook meestal luchtbellen achter. Men kan zich gemakkelijk voorstellen, dat het produkt lucht opneemt tijdens het vernevelen en drogen, dat zich immers geheel in lucht afspeelt. Anderzijds kan men vermoeden, dat vacuolen ontstaan als gevolg van kookverschijnselen in de drogende druppels (de ingaande drooglucht heeft een temperatuur boven 150 °C). Zulke vacuolen zouden dan aanvankelijk geen lucht bevatten.

De behoefte om de hoeveelheid lucht in de vacuolen te meten, bracht vele analytisch-technische problemen met zich mee, maar nadat de methode ontwikkeld was, kon het z.g. restgasvolume (het volume van het gas dat uit het poeder kan worden geïsoleerd) met dezelfde nauwkeurigheid worden bepaald als het vacuolenvolume.

Om een indruk te krijgen van het restgasvolume in vers bereide poeders en de wijzigingen die daarin optreden bij bewaring, werd een proef uitgevoerd met een zestal poeders. Daarbij bleek o.a. dat in 'drukpoeder' (verkregen door drukverstuiving) de gemiddelde luchtdruk in de vacuolen doorgaans beneden 0,2 kg/cm^2 ligt, terwijl deze in 'wielpoeder' (centrifugaalverstuiving) meestal rond 0,5 kg/cm^2 bedroeg. Een vrij diepgaande analyse van de zuurstof- en stikstofpenetratie tijdens deze proef leerde, dat zuurstof aanzienlijk sneller binnendringt dan stikstof en dat een laag vetgehalte in het produkt de penetratie sterk vertraagt.

3.2 Een hypothese omtrent valcuolenvorming (artikel III)

Een aantal sterke aanwijzingen omtrent het mechanisme van vacuolenvorming werd verkregen door het verband na te gaan tussen bepaalde procesvariabelen enerzijds en de volumina van vacuolen en rest-gas anderzijds.

Zo bleek dat het restluchtvolume (in vers poeder bestaat het restgas uit lucht) wel afhankelijk is van de eigenschappen van de te drogen vloeistof, en ook van de omstandigheden tijdens het vernevelen, maar niet van de omstandigheden tijdens de daarop volgende droging. Het restluchtvolume nam vooral af bij stijgende viscositeit van de vloeistof en het was voor wielverstuiving veel groter dan voor drukverstuiving. Het vacuolenvolume was altijd groter dan het restluchtvolume en het onderlinge verschil werd vooral bepaald door de droogomstandigheden: bij hogere inlaattemperaturen van de drooglucht nam het vacuolenvolume toe.

Hieruit kwam het volgende beeld naar voren: vacuolen bestaan uit luchtbellen die vóór de eigenlijke droging in de vloeistof geraken en tijdens het drogen nog uitzetten. Het vernevelen gaat blijkbaar gepaard met 'schuiming' en de mate van 'schuimvorming' hangt af van het type vernevelaar en van de vloeistof-eigenschappen, waaronder vooral de viscositeit. Het uitzetten van de luchtbellen wordt verklaard uit het krimpen van de drogende vloeistof. Dit klinkt tegenstrijdig, maar men moet zich voorstellen, dat tijdens de zeer snelle droging het oppervlak van de druppels verstart ('korstvorming') zoals door andere onderzoekers reeds was gevonden. Als er dan nog water verdampt uit het inwendige, terwijl de buitenkant niet meer krimpt of indeukt, wordt het volumeverlies binnen in de druppel gecompenseerd door expansie van de luchtbel(len). Dit mechanisme treedt sterker op, naarmate de droging sneller geschiedt (hogere luchttemperatuur).

Aldus konden de eerdergenoemde waarnemingen verklaard worden.

3.3 Nadere aanwijzingen en proef op de som (artikel IV)

Uit de voorgaande proeven waren reeds aanwijzingen verkregen, die er op wezen, dat de luchtinslag plaats vindt terwijl de vloeistof door de verstuiver stroomt, dus vóórdat ze in druppeltjes uiteenvalt. Om hieromtrent zekerheid te verkrijgen, werd in de verschillende verstuivers de lucht verdreven door koolzuurgas in te leiden. In de aldus bereide poeders vonden we dan inderdaad voornamelijk koolzuurgas in plaats van lucht.

Inmiddels was uit de hypothese reeds de conclusie getrokken, dat vacuolenvorming geheel zou kunnen worden voorkomen door de opname van gasbellen in de vloeistof te vermijden. Dit werd gerealiseerd door stoom in plaats van koolzuurgas in de verstuiver te injecteren. Er konden dan wel waterdampbellen in de vloeistof geraken, maar deze zouden daar snel condenseren. Inderdaad konden op deze manier vrijwel vacuolenvrije poeders worden bereid met elk type verstuiver. Deze gemodificeerde werkwijze die de naam 'luchtvrije verneveling' kreeg, trekt in de praktijk veel belangstelling.

Wellicht zal het ook mogelijk blijken om de lucht uit de verstuiver te verdrijven met vloeistof in plaats van stoom.

3.4 Nader onderzoek (artikelen V en VI)

Experimenteel was aldus het ontstaan van vacuolen genoegzaam verklaard, maar toch werd daarnaast ook nog getracht om vanuit een theoretische benadering het proces beter te begrijpen. Hierbij bleek, dat de luchtinslag naar alle waarschijnlijkheid kan worden beschreven met de z.g. Kelvin-Helmholtz-instabiliteit, die kan optreden aan het lucht-vloeistof-grensvlak in de verstuivers.

Ook kon uit theoretische overwegingen worden afgeleid, dat de spontane vorming van dampbellen (koken) in de drogende druppeltjes nauwelijks een rol kan spelen. Dit stemt overeen met de resultaten van het luchtvrij vernevelen.

Een ander interessant aspect van het verstuivingsdrogen is het temperatuurverloop in de drogende druppeltjes, ook al heeft dit met vacuolenvorming slechts zijdelings te maken. Ook hieromtrent werden proeven genomen, waarbij de tijdens het drogen optredende thermische inactivering van enzymen werd gemeten, waarvoor alkalische fosfatase en stremsel werden gekozen. De resultaten hiervan, aangevuld met andere gegevens, maakten het mogelijk om de 'drooggeschiedenis' van druppeltjes globaal grafisch weer te geven (het verloop van vochtgehalte en temperatuur als functie van de tijd). Er werden sterke aanwijzingen verkregen, dat het grootste deel van de waterverdamping plaats vindt bij zeer gematigde druppeltemperaturen, waarbij kookverschijnselen niet te verwachten zijn.

Tenslotte zij nog vermeld, dat tijdens het onderzoek op vele manieren is gebleken, hoezeer individuele deeltjes kunnen verschillen in diverse eigenschappen, zoals grootte, vorm, oppervlaktestruktuur, breekbaarheid etc. Ook het vacuolenvolume van afzonderlijke deeltjes varieert sterk, en wel volgens bepaalde patronen die vooral samenhangen met het type verstuiver.

4 Summary

4.1 Introduction

Spray-dried powder particles are not usually solid, but hollow, because they contain vacuoles. The presence of vacuoles is a disadvantage, for instance, with gas packing and 'instantization' of the product.

The mechanism of vacuole formation had not seriously been studied, even though several empirical data were available. Theoretical calculations and model experiments have also yielded certain data. However I decided to investigate vacuole formation by a mainly experimental approach, making use of the modified pilot spray drier, available at the Dairying Laboratory of the Agricultural University, where these studies were carried out.

4.2 Methods

Most of the experiments consisted of spray drying concentrated skim milk under various conditions. Atomization took place with rotating discs, high pressure nozzles and two-fluid atomizers.

Of the different analytical techniques used in these studies, microscopy was most important. The development of a new method for measuring the residual gas volume of spray powders was of paramount importance. Several other new methods were employed, such as the measurement of residual carbon dioxide volumes and the application of density gradients for studying the density distribution over individual particles.

4.3 Results and discussion

4.3.1 The residual gas volume (papers I and II)

Since atomization and spray drying take place in the presence of air, vacuoles might be just air bubbles. On the other hand boiling phenomena inside droplets could cause vacuole formation. Thus the amount of air present in the vacuoles immediately after drying, was measured.

It was found that the initial air pressure in the vacuoles was always well below atmospheric. Further measurements during storage of the powders yielded a better insight into the penetration of oxygen and nitrogen into milk powders.

4.3.2 A model on vacuole formation (paper III)

A study of the relationships between certain process variables and the volumes of vacuoles and air resulted in some valuable indications. The volume of residual air was a function of properties of the feed liquid (especially viscosity) and of the conditions during atomization. This suggested a process of 'foaming' that occurs during atomization.

The vacuole volume was always larger than the residual air volume and the mutual difference mainly depended upon the drying conditions: higher air temperatures resulted in larger vacuole volumes. Apparently the air bubbles incorporated into the feed liquid during spraying, expand during drying. This could be explained by 'case hardening'. Shrinkage of the droplet surface becomes increasingly difficult as the surface solidifies during drying. The removal of water from the droplet's interior will then cause the air bubbles to expand.

4.3.3 Further indications and proof (paper IV)

Carbon dioxide was flushed into the various atomizers. Powders prepared in this way were found to contain mainly this gas rather then air.

When steam was introduced into the atomizers instead of carbon dioxide, the powders contained hardly any vacuoles. Apparently the steam bubbles condensed before they could cause vacuole formation.

This modified process was called 'air-free atomization' and is expected to be applied in practice in the near future.

4.3.4 Other aspects (papers V and VI)

In addition to the experimental studies some brief theoretical considerations proved useful. The incorporation of air during atomization as well as the absence of spontaneous boiling during drying agreed with theoretical expectations.

The results of experiments on enzyme inactivation during spray drying, together with a combination of literature data, allowed an approximation of the 'drying history' of droplets. There were clear indications that most of the water evaporates while the droplet temperature is rather low.

Individual powder particles may differ in many properties. The distribution of the vacuole volume among particles shows certain patterns that are primarily governed by the type of atomizer.

overdruk uit het
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24 (1970) *96–105*

A method for the determination of the residual gas volume in dried milk products.

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Summary

Studying the vacuoles inside milk powder particles and their development during the spray-drying process it was considered important to compare the vacuole volume with the volume of gas which can be isolated from a powder sample ('residual gas volume'). Since the available methods for measuring the residual gas volume were considered unsuitable for our purpose, a better method was developed. In a flask containing a weighed sample of powder, air is replaced by carbon dioxide. Ethanol and water are drawn into the flask to disintegrate the particles and liberate the residual gas. The headspace gas is transferred from the flask to a gas burette in which CO_2 is removed with alkali so that only the residual gas remains, which is measured at 20°C. The amount of oxygen present in this gas can easily be determined by means of pyrogallol. An evaluation of the method, including the pretreatment with CO_2, is given, yielding satisfactory results.

1 Introduction

1.1 General remarks

It is generally known that milk powder particles obtained by spray drying are not usually solid, but are hollow. The open spaces inside the particles are usually referred to as air cells, gas bubbles, enclosed gas, entrapped air etc. (1, 2). To anyone who investigates the way in which these 'cells' are formed, these names are not satisfactory because other possible causes of cell formation exist besides gas enclosement (3, 4). Also unsuitable are names such as pores and cavities (5) because they may suggest an open connection between these spaces and the external atmosphere, which is unusual in spray-powder particles. The most suitable term appears to be vacuoles, used by Hallquist et al. (6) and Buma (7).

The idea that vacuoles (ranging in volume from about 5 to 40 ml per 100 g powder) are filled with air of about atmospheric pressure is old and widespread (1, 2, 8, 10). This is not surprising, considering the microscopical appearance of the vacuoles (1) and experience with gas packing of whole milk powder (1, 2, 9). In most of the literature no distinction at all is made between the vacuole volume and the volume of gas present in powder particles. Thus 'air volumes' are often computed from particle densities (1, 3, 8, 11, 12).

On the other hand there are indications that the gas volume in milk powder can vary with time. Photographs published by Hallquist et al. (6) showing gas bubbles emerging from milk powder particles suggest that the gas volume in four-hour-old milk powder is many times larger than in freshly prepared powder. If this was true in general, then the presence of air in older powder would be of little significance for explaining the process of vacuole formation.

Our present purpose being to elucidate this latter process, we reasoned that an accurate comparison of the volumes of vacuoles and gas should be useful, particularly if freshly prepared powders were analysed. Satisfactory methods are now available for measuring the volume of vacuoles per unit weight of milk powder (7). However the assessment of the gas volume still presents problems.

1.2 Existing methods

In 1944 Muers and Anderson (13) published an 'ebullition method' for measuring the gas volume contained in powder particles.

A suspension of the powder in propanol is introduced into boiling water and the liberated gas is transferred to a measuring tube. Apart from operational difficulties it is stated that blanks are high and the limit of accuracy is 0.03 ml/g, which is poor.

Better results were obtained by Rutgers (14) who was interested in measuring the residual gas which remains in milk powder after a brief evacuation. His method involves the evacuation of a 20-g milk powder sample contained in a 250-ml flask which is fitted with an 8-ml gas measuring tube. Cold and hot water are drawn into the bottle until the powder has dissolved and atmospheric pressure has been reached. The volume of gas is read in the graduated tube. The blank value (highly dependent upon the vacuum attained) usually varied from 4 to 5 ml per 100 g powder. No measurements involving the addition of known volumes of air were reported. The variation among duplicate determinations was usually below 1.5 ml per 100 g, but sometimes it went up to 4 ml. For these reasons the accuracy and the reliability of this method were considered insufficient for the purposes described above and a new method was developed.

2 Method

2.1 Principle

The method to be presented in this paper is based on the same principle e.g. the liberation of gases by dissolving the powder after evacuation, but the actual procedure is different. In the flask containing the sample, air is replaced by carbon dioxide by successive partial evacuations. At a later stage the CO_2 present in the sample flask (about 170 ml) is removed from the residual gas by means of alkali. This reduces the blank value and makes it independent of small variations in the vacuum attained. The admissibility of this procedure will be discussed in Section 3.1. A very fast disintegration of the powder particles is promoted by adding hot ethanol prior to the water. Clumping of the powder is easily avoided in this way.

A further new feature of the method is the rapid measurement of oxygen in the residual gas. After the gas has been transferred to a gas burette the alkaline solution in the burette that has already removed the CO_2 can also absorb the oxygen if some pyrogallol is introduced.

Finally it may be noted that the pretreatment with CO_2 will eliminate most of the gas that is probably adsorbed at the powder particle surface. Thus only the gas inside the vacuoles and most of the gas dissolved in the solid phase of the particles are measured, which we will define as residual gas. Of course any CO_2 which might be present in the powder is not measured.

2.2 Method of analysis

2.2.1 Pretreatment of sample (see Fig. 1). In a dry weighed 1.5-litre flask A about 100 ml of powder is weighed with an accuracy of ± 0.5 g. The flask is tightly closed with a rubber stopper in which a glass tube and a 3-way stopcock

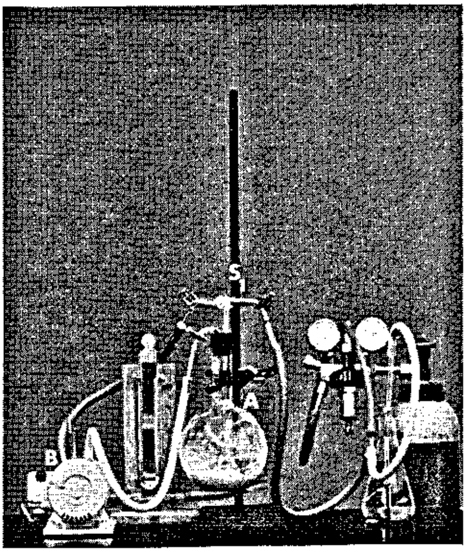

Fig. 1. Pretreatment of the sample.

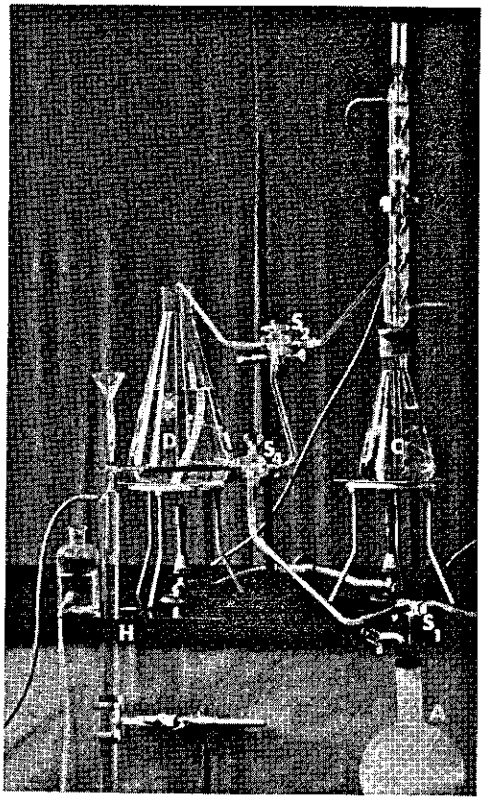

Fig. 2. Adding the solvents.

S_1 are fitted, and flushed during 30 sec with carbon dioxide containing over 99% CO_2. Immediately after evacuation (vacuum pump B) to 40 mm Hg, carbon dioxide is introduced until atmospheric pressure is reached. This evacuation and gassing are repeated and the pressure is then reduced to 80 mm Hg. This pretreatment should be completed within 3 minutes.

2.2.2 Addition of solvents (see Fig. 2). The dissolving medium is prepared by boiling ethanol and tap water in separate conical flasks C and D for at least 15 minutes. The liquids can be discharged via a 3-way stopcock S_2. Flask A is connected with S_2 via S_1 and S_4 and after the tubing has been completely filled with the hot ethanol about 200 ml is drawn into flask A. The mixture is shaken and the hot water is then introduced. Burette H and stopcock S_4 are used in calibration experiments (see Section 3.5).

2.2.3 Transferring and measuring the gas (see Fig. 3). When the stream of water has almost stopped cock S_1 is closed and connected to a water-jacketed

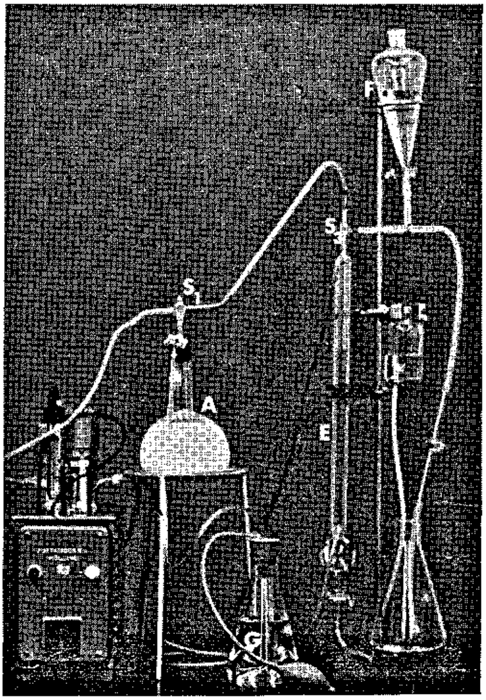

Fig. 3. Transferring and measuring of the gas.

(20°C) 50 ml gas burette E which is filled with a 2% aqueous KOH solution. The burette is maintained at a temperature of 20°C by circulating thermostatically controlled water. The specially designed burette has a 100-ml bulb at its lower end, in which a temporary excess of gas (CO_2) can be held. From a reservoir F containing boiled water the tubing to S_1 is filled with water. By turning S_1 the flask is connected with F until pressure equilibrium is reached. S_3 is now turned to connect the flask with the burette. The headspace gas in the flask is then transferred quantitatively to the burette by pumping boiled water from reservoir G into the flask.

All operations from the addition of the ethanol until the transference of the headspace gas should be carried out in a constant length of time (6 minutes). Finally the burette is tilted a few times until all the CO_2 has been absorbed. After allowing some minutes for reaching temperature equilibrium the volume of gas in the burette is read with an accuracy of about 0.02 ml, corrected with a blank value and multiplied by a calibration factor $c = 1.06$ (see Section 3.5). The blank value accounts for the amount of gases in the CO_2 supply which are not absorbed in 2% KOH at 20°C. Let this percentage of impurities be N% (v/v), then the blank is calculated as:

$$B = V \times \frac{80}{760} \times \frac{N}{100} \text{ ml},$$

V being the volume of the closed flask minus the volume of the powder sample.

2.2.4 Measurement of oxygen. If the amount of oxygen present in the residual gas is to be measured, a small funnel is fitted on top of the burette after the total residual gas volume has been read. About 1 ml of a 25% solution of pyrogallol is carefully introduced and the burette is tilted 20 times. After a few minutes the reduction in volume, representing oxygen, can be read.

2.3 Notes

1. Wherever possible glass tubing must be used for making the necessary connections. Several transparent flexible tubes were tested for air tightness at 100°C, but none of these proved completely reliable.
2. The alkali solution in the burette must be saturated with air. It is prepared by mixing suitable amounts of demineralized water and a 40% potassium hydroxide solution. The diluted solution is kept at about 20°C for several hours until all air bubbles have disappeared.
3. If the composition of the gas drawn from the CO_2-cylinder varies with time, frequent determinations of N are needed. These are made with the gas burette while it is filled with water, introducing the calculated amount of KOH after 150 ml of gas have been drawn into the burette.
4. Fluctuation in barometric pressure can cause significant variations if the measured volume of gas exceeds 5 ml. In these cases a correction is applied on the basis of 760 mm Hg.

3 Results and discussion

3.1 Check of admissibility of pretreatment with CO_2

The purpose of the repeated evacuation in a CO_2-atmosphere is the removal of external air from the sample. Inevitably, however, some gas will also be drawn from the particles themselves. Therefore the pretreatment is an arbitrary one, aimed at a complete removal of external gas and at a minimal loss of gas from the interior of the powder particles. Thus it was considered necessary to check whether a prolonged evacuation would cause a significant loss of residual gas.

From a batch of whole milk powder, stored under dry air for one week, three samples were analysed on each of three successive days. After the second evacua-

Table 1. Residual gas volumes (ml/100 g) of whole milk powder obtained after varying evacuation times at 40 mm Hg.

Evacuation time (min)	Residual gas volumes		
	Exp. 1	Exp. 2	Exp. 3
0	10.1	9.8	9.6
3	10.4	9.6	10.0
10		9.2	9.4
30	8.8		

tion the samples were kept at a pressure of 40 mm Hg for 0, 3, 10 or 30 minutes according to Table 1.

From these figures it was concluded that no significant loss of residual gas occurs within a few minutes. Hence, it can be assumed that the normal pretreatment procedure does not remove any residual gas.

The oxygen content in the residual gas in all nine samples varied from 29 to 30%.

3.2 Blank values

Blank values, calculated as described above, were compared with measured blanks. These were obtained by the normal method of analysis, replacing the powder sample by a similar volume of small glass beads (100 ml).

Table 2 indicates that the calculated blank values are suitable, if deviations up to 0.2 ml are accepted.

Table 2. Comparison of measured blank values with those calculated from the impurity (N) of the CO_2 supply

Blank values (ml)		N (% v/v)
calculated	measured	
0.9	0.9	0.44
0.9	1.1	0.42
0.8	1.0	0.40
0.7	0.8	0.36
0.7	0.8	0.35

Table 3. Residual gas volumes (ml/100 g powder) in freshly prepared milk powder and during storage in CO_2 and air.

	Dried skim milk		Dried whole milk	
Fresh	0.6		1.2	
	0.4		1.0	
Storage time	Dried skim milk stored in		Dried whole milk stored in	
	CO_2	air	CO_2	air
2 days	0.0	0.7		
	—	0.7		
4 days			0.1	3.3
			0.2	3.0
15 days	—0.2	0.7		
	—0.1	0.9		
18 days			0.0	3.4
			—0.1	3.3
21 days		0.9		
		0.9		

3.3 Check of zero value

Since the accurate measurement of very small quantities of gas can be necessary, it is of particular importance that zero values are obtained for air-free powders. For this purpose spray powders were used containing far less than 1 ml vacuoles per 100 g, which were produced in our experimental spray dryer by using a modified atomization system. Some powder samples produced in this way were held either under a CO_2-atmosphere at reduced pressure or under dry atmospheric air, both at room temperature (see also Section 3.4). The residual gas volumes (ml/100 g powder) measured after different storage times are reported in Table 3 (see column CO_2).

Table 3 shows that approximate zero values are indeed obtained when dry whole or skim milk has been thoroughly de-aerated.

3.4 Dissolved air

Since the vacuole volumes in both powders (Table 3) were about 0.2 ml/100 g, the results obtained after equilibrating the powders with air give an indication of the amount of 'air' (or N_2, O_2) that can dissolve in the solid phase of the particles. For dried skim milk and dried whole milk at room temperature this amounts to about 0.7 and about 3.1 ml/100 g, respectively.

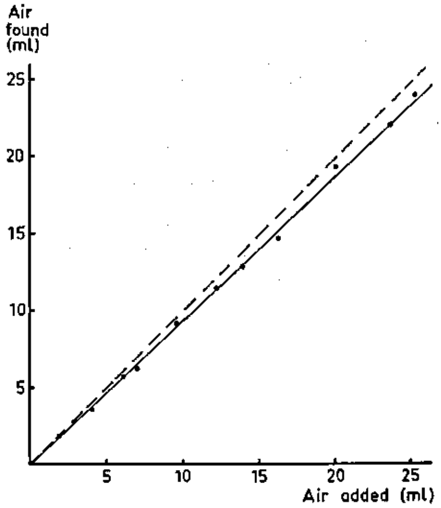

Fig. 4. Calibration data.

3.5 Calibration (see Fig. 2 and 4)

In Fig. 2 a gas burette H which is used for adding known volumes of air via stopcock S_4 to the sample flask can be seen. A number of measurements were made in which the ethanol addition was interrupted by adding air to a sample consisting of air-free (de-aerated) skim milk powder. The results are presented graphically in Fig. 1. There appears to be a certain loss of air which is roughly proportional to the amount of air added. This may indicate solution of air in the ethanol-water mixture, since in this case the amount of air dissolved should be proportional to the air pressure in the flask. Mathematical treatment of these data yields a calibration factor $c = 1.06$ by which the results should be multiplied. The confidence limits for c are 1.047 and 1.078 (confidence coefficient 95%).

3.6 Accuracy

A sixfold analysis of a certain powder yielded residual gas volumes ranging from 4.3 to 4.5 ml/100 g. From these data a standard deviation $\sigma = 0.08$ ml/100 g was computed.

Additional data, obtained from 20 duplicate determinations in different samples, indicated that σ increased with increasing residual gas volumes. Taking gas volumes below 5 ml/100 g for the calculation (11 duplicates) a σ of 0.11 ml was found; when volumes from 5 to 22 ml/100 g were taken for the calculation (9 duplicates) a standard deviation of 0.41 ml/100 g was found.

4 Conclusions

The method requires a good deal of care and skill in operation. A trained person can analyse a sample in about one hour.

The procedure described is one which was arrived at after a certain period of development, and although further improvements may be possible the results obtained so far are considered quite satisfactory for our purpose.

A future paper will deal with applications of this method aimed at the improved control of powder properties.

Samenvatting

J. G. P. Verhey en W. L. Lammers, Een methode voor het meten van het 'rest-gas-volume' in droge melkprodukten

Bij het bestuderen van de vakuolenvorming in melkpoederdeeltjes tijdens het verstuivingsdrogen werd het van belang geacht het vakuolenvolume te vergelijken met de hoeveelheid gas die uit een monster poeder geïsoleerd kan worden ('rest-gas-volume').

Aangezien de reeds bekende methoden om het rest-gas-volume te meten ongeschikt voor ons doel werden bevonden, werd een betere methode ontwikkeld.

Een gewogen monster van het poeder bevindt zich in een kolf waarin de lucht wordt vervangen door koolzuur. Ethanol en water worden in de kolf gezogen om de poederdeeltjes te desintegreren en het rest-gas vrij te maken. Het gas wordt dan overgebracht naar een gasburet waarin het koolzuur wordt gebonden met alkali zodat alleen het rest-gas overblijft, dat bij 20°C wordt gemeten. Op eenvoudige wijze kan in dit gas ook nog de hoeveelheid zuurstof worden bepaald met behulp van pyrogallol.

Er wordt een evaluatie gegeven van de methode, met inbegrip van de voorbehandeling van het monster. De resultaten daarvan zijn bevredigend.

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Air penetration into milk powder

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Abstract

Centrifugal spray and pressure spray milk powders with various fat contents were stored in air at room temperature. From repeated measurements of the residual gas and oxygen volumes of each powder during a period of about 3 months, oxygen and nitrogen penetration curves were obtained. Equilibrium residual volumes of both gases were derived in a general manner and the gas penetration rates were related to the concentration differences. It was found that the gas volumes in freshly prepared disc spray powder were about half of the vacuole volume, whereas the vacuoles of fresh pressure spray powder contained about 20% air. Oxygen penetrated the powders faster than did nitrogen and the gas penetration rates were higher when the powders contained more fat. By considering the large variations in the structure of individual powder particles the results could be explained in a qualitative way.

1 Introduction

The desirability of storing whole milk powder in an oxygen-free atmosphere has initiated a number of studies, aimed at producing the optimum gas-packing conditions. In some of these studies (1, 2) the volume of oxygen present inside the powder particles was calculated from the vacuole volume of the powder, assuming that the vacuoles were filled with air of atmospheric pressure or slightly lower. Other workers (3, 4), however, noted a smaller oxygen desorption if freshly prepared powder was gas-packed, which yields circumstantial evidence for the existence of sub-atmospheric pressures in fresh powder particles. No direct experimental proof of this latter phenomenon has so far been presented.

In a previous paper (5) we described a method for the determination of the residual gas volume in milk powders. It will be remembered that the residual gas is isolated from the powder particles by dissolving them in boiling water. This method, which includes the measurement of residual oxygen, allows a rather straightforward approach to the question raised above.

On the other hand, knowledge of the residual gas volume in fresh powder is of great importance in our studies on vacuole formation. For that purpose it is also necessary to check whether any rapid changes in the residual gas volume at the moment of sampling might hamper its determination. These were the first objectives of the experiment described in this paper.

By continuing the measurements for several months, we obtained valuable data on the oxygen and nitrogen penetration. Gas penetration in milk powder was studied previously by Berlin et al. (6, 7) who concluded that the process was to be interpreted mainly as a surface diffusion along the walls of extremely narrow micropores in the particle material. In their method, a volume of helium or nitrogen gas is admitted to a powder sample that has been thoroughly evacuated previously. A decreasing pressure in the system indicates gas penetration into the powder. Constant pressure was obtained within minutes for helium, but nitrogen penetrated far more slowly. The method gives no proof of the entire removal of nitrogen during evacuation. This causes some of the conclusions to become questionable.

Buma (4, 8, 9) studied the micropores in more detail, using the air comparison pycnometer in which the volume of a sample is measured after doubling the gas pressure. Again a drawback of the method is that only gas penetration is measured and not the actual residual gas volume. Buma concluded that the micropores were often wide enough to allow the extraction of fat from the interior of the particles by fat solvents.

It can be said that the existence of micropores in spray-dried milk particles has been well established. This implies that not only diffusion but also several types of flow are to be considered in connection with gas penetration.

2 Methods

2.1 Production and storage of powders

Milk powders containing < 1, 10 or 25% fat were prepared from batches of 80 kg milk that were standardized at the required fat content and pretreated as follows. The skim milk was pasteurized at 72°C for 14 seconds; the other batches were preheated for 20 seconds at 90°C and homogenized at 200 kg/cm^2.

Subsequently the liquids were concentrated to about 44% total solids in a batch evaporator, operating at temperatures below 45°C. The concentrates were then fed to the atomizer at 30–35°C and care was taken to avoid any air incorporation in the liquids.

From each batch of condensed milk two powders were prepared, viz by centrifugal and by pressure atomization. Inlet and outlet air temperatures were 154 and about 98°C, respectively.

The drying chamber of our experimental drying plant (Fig. 1) was originally

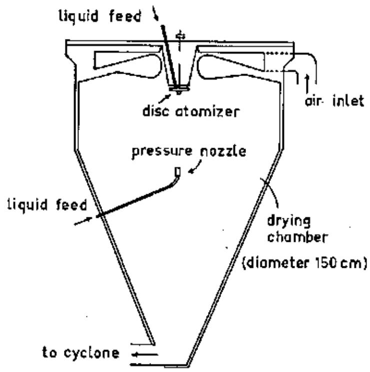

Fig. 1. Diagram of the spray drier.

designed for centrifugal disc atomization, but it appeared possible to use pressure nozzles as well. The maximum capacity is about 25 kg water evaporation per hour.

All of the powder produced is collected with a single cyclone.

The sampling of 'freshly prepared' powder took place during each production run. In these cases a clean collecting vessel under the cyclone was flushed with CO_2 during a three-minute sampling period. From this vessel duplicate samples were weighed into sample flasks within a few minutes.

The other powder samples were not treated with CO_2 and they were stored for several months in air at 20°C in well sealed containers of adequate size, such as dessicators and jars. The changes in moisture content and vacuole volume during storage were negligible.

2.2 *Measurement of residual gas volume*

Immediately after production of the powders and after different storage times the volumes of residual gas and oxygen were measured in duplicate according to the method published (5).

2.3 *Measurement of vacuole volume*

Apparent average particle densities (ϱ_a) were measured with the air comparison pycnometer (Buma, 4, 9). True densities (ϱ_t) were computed from the chemical composition of each powder, using the data suggested by Buma (10). The vacuole volumes, expressed in the same unit as the residual gas volumes, are then given by

$$100 \left(\frac{1}{\varrho_a} - \frac{1}{\varrho_t} \right) \text{ ml/100 gram powder}$$

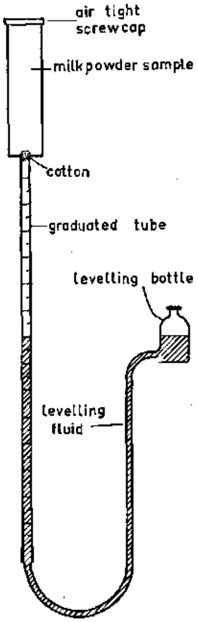

Fig. 2. Apparatus used for the direct measurement of air uptake.

2.4 Direct measurement of air uptake

A very simple apparatus for the direct measurement of the volume of air that is absorbed by a powder sample under atmospheric conditions is depicted in Fig. 2. It consists of a plastic powder container with a graduated tube, in which atmospheric pressure is maintained by means of a levelling bottle. The levelling fluid should be saturated with air and it should neither absorb nor emit any water vapour. We used mixtures of glycerol and water having about the same equilibrium relative humidity as the powder. A number of such containers are placed in a constant temperature room and filled with 50 g powder samples at room temperature (20°C). Volume readings (at atmospheric pressure) are taken immediately after filling and daily or weekly later on. The readings taken from an empty container that is included in the experiment are used to compensate for changes in temperature and barometric pressure. Knowing the volume of each container as well as the powder volumes, the gas volume reduction in each container can be expressed as ml air penetrating 100 g powder.

2.5 Measurement of equilibrium relative humidity of milk powders

The procedure outlined in Section 2.4 necessitates the knowledge of the equilibrium relative humidity of dried milks.

As a simple routine technique for measuring this property the following procedure was adopted. Six glycerol-water mixtures are prepared in such a way that the resulting liquids have equilibrium relative humidities ranging from 15 to 40%. From each liquid 0.50 ml is transferred to a 1-ml Durham tube. These six small tubes are placed vertically in six 25-ml culture tubes which have been nearly filled with the powder. The tubes are closed with a rubber stopper and kept at a constant temperature (14°C in our case) for a few days. Any temperature changes during these operations must be avoided.

After a few days the changes in refractive index of the glycerol solutions are measured and plotted against the original equilibrium relative humidities of the solutions. By means of graphical interpolation the equilibrium relative humidity of the powder is easily obtained with an accuracy of about 1%.

3 Results and discussion

3.1 General

The data given in this paper are typical of the powders produced in our laboratory. They show a rather low rate of gas penetration. In this respect large variations exist among different powders as will be discussed below.

Therefore it is stressed that our results cannot be expected to have an absolute validity for other equipment and process conditions.

3.2 Gas absorption measurements

In our first experiments, gas absorption curves of different powders were determined by means of the direct measurement of gas uptake (see Section 2.4). Some typical curves are shown in Fig. 3. The rate of gas absorption appears to increase with increasing fat content. Pressure spray skim milk powder exhibits an extremely low rate of gas absorption.

It should be noted that although these measurements are carried out under fairly ordinary storage conditions, they still have the important disadvantage that the initial residual gas volume is not measured. By means of illustration, let us consider a cengrifugal spray skim milk powder, which in 6 weeks absorbs 8 ml gas/100 g powder. Since this powder contains 50 ml vacuoles/100 g, the initial gas volume may have been anything between zero and about 40 ml/100 g. Consequently it is not possible to relate the gas penetration rate to a concentration difference. If the curves would level off within a reasonable time, more information would be available, but in our experience the equilibration with atmospheric air may take years for skim milk powders and many months for whole milk powders.

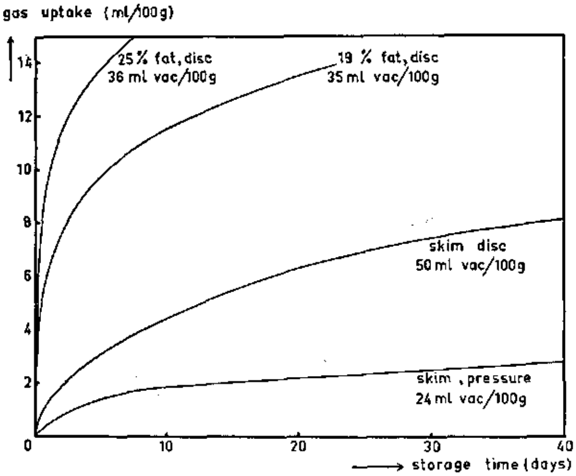

Fig. 3. Gas uptake curves obtained with the apparatus shown in Fig. 2. Fat content of the powders, atomization system and vacuole volumes are indicated.

Another disadvantage of this type of measurement is that the first reading cannot be taken until the fresh powder has been cooled to the desired temperature, which in our case took about 15 minutes.

Both objections can be effectively dealt with by estimating the residual gas volume rather then gas absorption.

3.3 Outline of new experiment

In designing the experiment reported below, two variables were chosen, fat content and atomization system. This choice was based upon the experience that these parameters would lead to interesting differences both in initial residual gas volume and in gas penetration rate. Since all other process conditions were kept the same, the fact had to be accepted that changes in the fat content would cause the exit air temperature and the moisture content to change accordingly. The analytical data obtained in this experiment have been collected in Table 1. For a systematic analysis of these data, let us first consider the freshly prepared powders.

3.4 Initial residual gas volume

The vacuole volumes of the powders D (disc atomization) are larger than those of the powders P (pressure atomization) which is a common observation.

The powders D show initial residual gas volumes that are about half of the corresponding vacuole volumes, whereas the residual gas volumes of the pow-

Table 1. Residual gas volumes (rgv) and oxygen volumes (both in ml/100 gram powders) of six milk powders during storage in air at 20°C.

Fat in powder (%)	< 1				10				25			
Atomization	disc		presssure		disc		pressure		disc		pressure	
Sample code	D_1		P_1		D_{10}		P_{10}		D_{25}		P_{25}	
Moisture (%)	3.7		2.9		2.7		1.8		1.4		1.1	
Vacuole volume (ml/100 g)	28.1		21.3		30.1		22.5		31.2		20.8	
Storage time (days)	rgv	O_2	rgv	O_2	rgv	O_2	rgv	O_2	rgv	O_2	rgv	O_2
0	14.4	3.0	3.0	0.8	15.3	3.2	3.7	0.8	13.9	3.2	4.5	1.3
1					18.7	4.4	5.6	1.6	20.2	5.6	8.3	2.8
2	17.2	4.1	4.0	1.2								
3									22.2	6.3	9.9	3.5
4					20.4	5.2	6.7	2.2				
8	18.3	4.6	4.7	1.5								
10									24.7	6.8	11.4	4.1
15					22.3	5.9	8.7	3.4				
21									26.5	7.0	13.2	4.8
23	19.8	5.3	6.4	2.5								
35					24.8	6.6	10.7	4.1				
44	21.2	5.8	7.4	3.1								
56									29.9	7.5	17.2	5.4
61					26.3	6.6	12.4	4.4				
67	22.0	5.9	8.2	3.3								
92					27.1	6.7	13.4	4.6				
108									31.1	7.3	19.5	5.5

ders P amount to only 15–20 % of the corresponding vacuole volumes. Assuming that almost the entire residual gas is present as gas inside the vacuoles, this means that the pressure in the vacuoles averages about 0.5 kg/cm^2 in the powders D and below 0.2 kg/cm^2 in the pressure spray powders. This fact will be dealt with in detail in future papers.

Considering the oxygen volumes present in the residual gas, it can be tentatively concluded that the initial residual gas is air.

3.5 Gas penetration rate; general observations

In Fig. 4 residual gas volumes are presented graphically, together with the corresponding vacuole volumes (right hand axis). Fig. 5 shows the oxygen volumes and, for comparison, the vacuole volumes multiplied by 0.21. In the same way 'nitrogen' volumes are plotted in Fig. 6, obtained by subtracting oxygen volumes from the corresponding residual gas volumes. In this case the vacuole volumes were multiplied by 0.79 to yield a value for comparison. Fig. 4 merely demonstrates that the duration of this experiment was insufficient for any of these powders to reach equilibrium. Oxygen volumes did reach practically constant values in some cases (D_{25}, D_{10} and P_{25}) but the penetration rate of nitrogen is slower. This difference causes the oxygen content of the

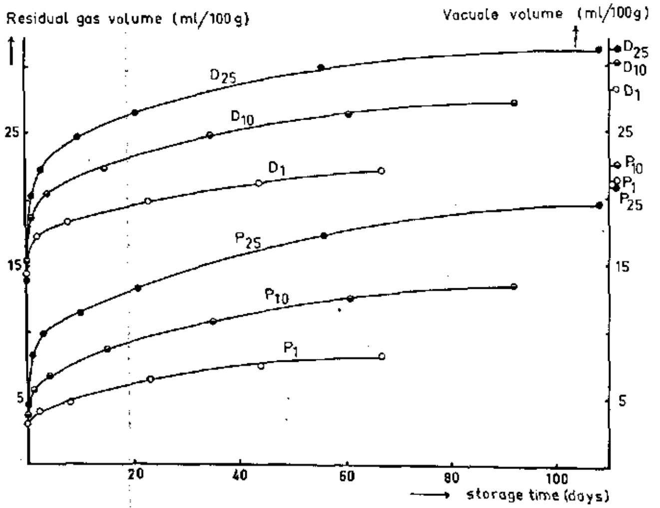

Fig. 4. Residual gas volumes of different powders during storage. The corresponding vacuole volumes are shown at the right hand axis.

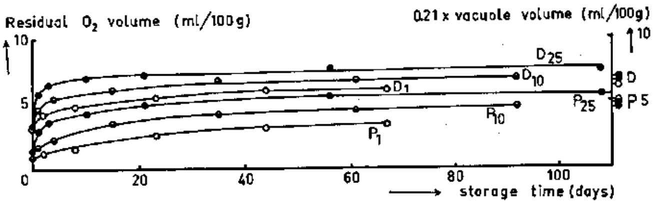

Fig. 5. Residual oxygen volumes of different powders during storage. Values for comparison are shown at the right hand axis.

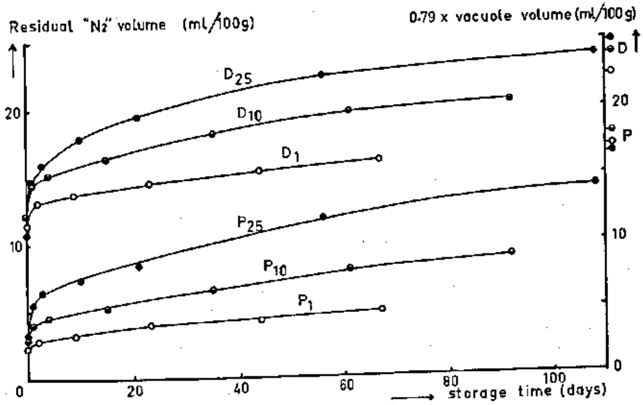

Fig. 6. Residual 'nitrogen' volumes of different powders during storage. Values for comparison are shown at the right hand axis.

residual gas to rise considerably above 21 %. Especially in the pressure spray powders values of well over 30 % were found within a few days, and for powder P_1 the residual gas contained 42 % oxygen after 44 days, as can be readily calculated from Table 1. A similar phenomenon was observed by Buma (9).

3.6 *Estimation of equilibrium residual gas volume*

A more thorough treatment of the data shown in Fig. 5 and 6 would be possible if any volume V_t on these curves could be related to a final equilibrium volume V_m. Since in most cases no equilibrium is reached during this experiment, V_m has to be arrived at by calculation.

It will be noted from Fig. 5 that the oxygen volumes eventually exceed the 'theoretical' values given at the right hand axis. This could be caused by adsorption and dissolution. It was tried to relate the 'excess' oxygen volumes to the fat content of the powders. For the volume of oxygen dissolved in 100 g fat in the powders D_{25}, D_{10} and P_{25} values of 4.0, 4.5 and 4.6 ml were found, respectively. These figures show fair agreement but dissolution of oxygen in the non-fat fraction of the powder should not be disregarded. Therefore it is useful to compare these findings with literature data. Adsorption of air onto the particle surface can be neglected since we found no relationship between the residual gas volume and the surface area of size fractions of powders produced by means of air-free atomization (11).

According to Bailey (12) the solubility coefficient S (v/v) of pure oxygen in a unit volume of several fats, including butterfat, is given by

$S = 0.1157 + 0.000443\ t$,

t being the temperature in °C. For oxygen at 20°C and 0.21 kg/cm^2 this yields a volume of 2.8 ml dissolving in 100 g fat. For nitrogen (20°C and 0.79 kg/cm^2) 5.9 ml/100 g is calculated from a similar formula. The actual solubility of oxygen is milkfat in thus twice as high as the solubility of nitrogen which agrees with data given by Buma (9).

Far larger volumes of oxygen can be consumed by fat oxidation (Koops, 13) but this oxygen can scarcely be measured in our experiments. This means that the oxygen penetration rate is in fact higher than can be detected from our data. It also implies that an oxygen concentration of 21 % inside the vacuoles will not be reached as long as fat oxidation continues. The conditions in milk powder, however, are far less favourable for chemical oxygen consumption than in Koops' experiment. Consequently the eventual oxygen pressure in the vacuoles will be quite close to atmospheric, which is also indicated by Fig. 5.

Taking Bailey's value of 2.8 ml oxygen dissolving in 100 g fat, the oxygen volumes emanating from the non-fat fraction of the powders D_{25}, D_{10} and P_{25} can be calculated to be 0.40, 0.19 and 0.60 ml/100 g non-fat powder, respectively. These values agree rather poorly, but their contribution being small, it is tolerable for our purpose to use an average of 0.4 ml/100 g non-fat powder when computing V_m.

In the case of nitrogen no data are available from our experiment, since equilibrium is not reached in any powder (Fig. 6). In a previous paper (5) however, it was reported that about 3.1 ml of 'air' was present in the solid phase of whole milk powder (28 % fat), and about 0.7 ml in the solid phase of skim milk powder. This was measured in high density powders, prepared by means of air-free atomization (11). These powders show a high rate of gas uptake; equilibrium was practically reached within about 2 weeks. Using the oxygen and nitrogen solubility data derived above from Bailey's formulae, it is found that in this whole milk powder 0.8 ml oxygen and 1.7 ml nitrogen/100 g were dissolved in the fat phase. The balance (3.1–0.8–1.7 = 0.6 ml 'air')

Table 2. Residual oxygen and nitrogen volumes V_m (ml/100 g powder), calculated for equilibrium conditions.

	D_1	P_1	D_{10}	P_{10}	D_{25}	P_{25}
O_2	6.3	4.9	6.9	5.3	7.5	5.4
N_2	22.7	17.3	24.8	18.8	26.4	18.2

amounts to 0.8 ml 'air'/100 g non-fat powder. This is reasonably close to the value of 0.7 ml found in the skim milk powder. Taking 0.8 ml 'air' as an average of both findings and subtracting the oxygen value derived above (0.4 ml) we find an equilibrium nitrogen volume of 0.4 ml/100 g non-fat powder.

Although the foregoing computations are not very accurate and sometimes rather arbitrary, they appear to be the best we could do. They find some justification in the fact that slight differences in the actual value of V_m would not materially alter the conclusions.

Summarizing, the values for V_m, shown in Table 2, are computed for oxygen and nitrogen, respectively, according to:

$V_m(O_2) = 0.21\ V_v + 2.8\ F + 0.4\ (1\text{-}F)$

$V_m\ (N_2) = 0.79\ \ V_v + 5.9\ F + 0.4\ (1\text{-}F)$

where V_v represents the vacuole volume (ml/100 g) and F is the fat content (g/g) of the powder.

3.7 Further examination of gas penetration

The curves in Fig. 5 and 6 were graphically differentiated at certain values of time t ranging from $\frac{1}{2}$ to 40 days, yielding the average gas flux $\bar{f}$ into the powder particles at that moment ($\bar{f} =$ dv/dt). The corresponding residual oxygen and nitrogen volumes V_t were also read from the curves. At any time t the parameter $(V_m—V_t)/V_m$, multiplied by 0.21 or 0.79, represents the average pressure difference $\overline{dp}$ between the interior of the particles and the external oxygen or nitrogen, respectively (any differences between the volumes of dissolved gas included in V_m and V_t, are disregarded).

For a single particle with one central vacuole a certain relationship may be expected between the flux f and the pressure difference dp across the particle wall, depending upon the dominant transport mechanism (diffusion, flow, etc.). Fig. 7 shows a plot of $\bar{f}$ as a function of $\overline{dp}$, as it appears from our data. It seems evident that the shape of these curves cannot be explained by any of the common transport formulations. It appears amazing, for instance, that the nitrogen flux drops by 90% as $\overline{dp}$ decreases by 5%.

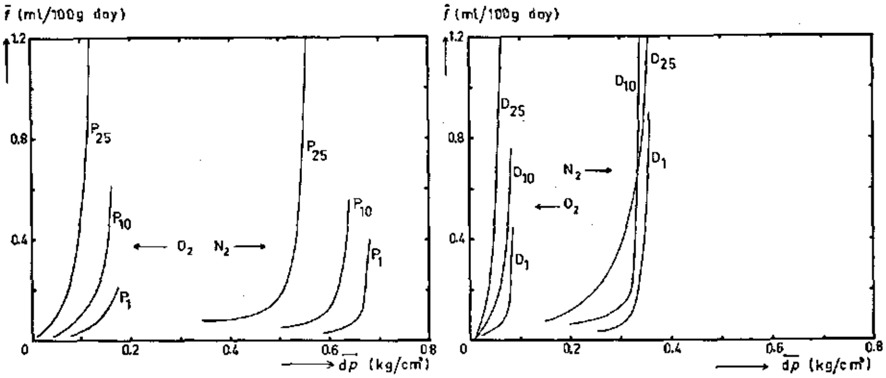

Fig. 7. Oxygen and nitrogen flux $\bar{f}$ plotted against the corresponding pressure difference $\overline{dp}$.

From microscopical observation, however, it is evident that the individual powder particles are very different in many ways such as size, shape, vacuole volume and wall thickness. Hence the volume V_m, and in particular the flux f, will vary widely among individual particles. This was also recently noted by Buma (9). Therefore, high values of $\bar{f}$ must be expected during the first hours and days of storage, but after the most accessible particles have been filled, this value will decrease considerably.

It is quite illustrative to compute the apparent 'permeability' P of the powders, expressed by means of the parameter

$$P = \bar{f}/\overline{dp}$$

Fig. 8 shows plots of P against log time. It will be noted that the curves cover the time interval from $t = \frac{1}{2}$ to 40 days. In this period the apparent 'permeability' decreases more than tenfold in many cases.

Considering these data, it seems impossible to say which transport law governs the gas penetration. An attempt could be made to fit the data into a certain equation by inserting a series of diffusion coefficients or pore lengths, etc., but in that way almost any model might be made to fit, as long as we have no reliable data on the distribution of such parameters over the different powder particles. Nevertheless we will return to this subject in the next section.

When, as in Fig. 8, the centrifugal and the pressure spray powders are compared with each other, it is observed that the latter powder has the lowest permeability for both gases. This may be understood from the differences in structure of the particles, as they appear under the microscope. Generally, centrifugal spray powder particles contain several vacuoles, distributed through-

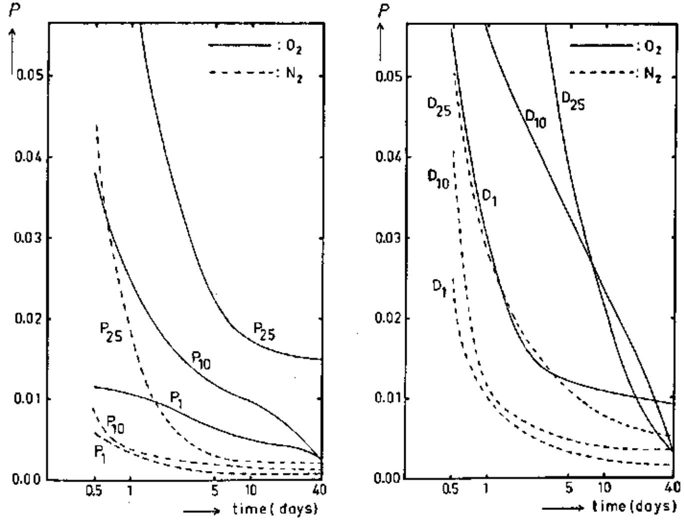

Fig. 8. Apparent 'permeability' ($P = \bar{f}/\overline{dp}$) for oxygen and nitrogen during storage of milk powders.

out the particle, whereas pressure spray powder particles contain very few vacuoles (if any), usually in the centre. This implies a greater average wall thickness in the latter powders.

3.8 Solid state diffusion

On the question of the transport mechanism involved in the gas penetration, a peculiar fact is yet to be discussed. The ratio of oxygen to nitrogen 'permeability' $P(O_2)/P(N_2)$, derived from the data of Fig. 8, is shown versus log time in Fig. 9. When this ratio equals 1, air of normal composition is being drawn into the powder. During the first days of storage, the ratio rises considerably. Except for powder D_1, a maximum is reached within 40 days, and finally the ratio again decreases in most cases.

The 'permeability ratio' does not show a consistent relationship with moisture and fat content of the powders. On the other hand, it may be significant that the curves of the pressure spray powders are more similar to each other than those of the disc spray powders. This may be related to the more complex structure of the latter powders, as was discussed above.

At first sight the height of the maxima in Fig. 9 is amazing because it can hardly be understood why oxygen would penetrate so much more easily than

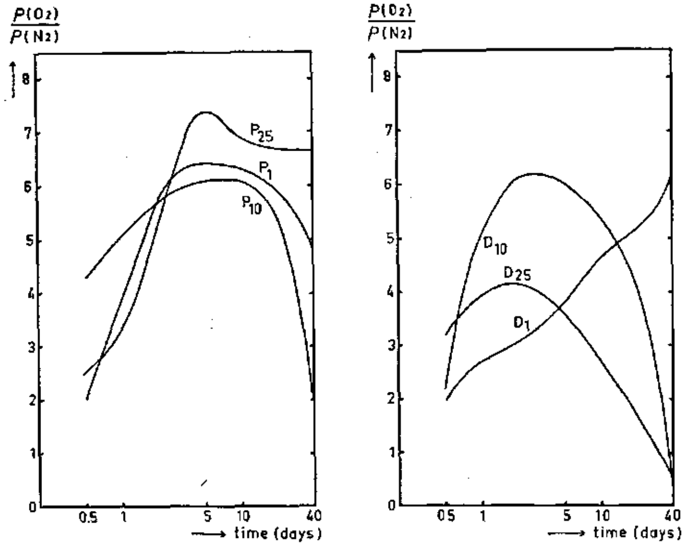

Fig. 9. Ratio of oxygen to nitrogen 'permeability' $P(O_2)/P(N_2)$ during storage of milk powders.

nitrogen does. A reasonable explanation, however, can be offered if it is assumed that the gas transport takes place by diffusion. This assumption is based primarily on the very low $\bar{f}$ values found after a few days of storage.

Dried milk may be considered to be somewhat analogous to polymers and the 'solid state diffusion' in these materials has received much attention during the past decades. The gas flux Q through homogeneous polymers is usually proportional to the diffusion coefficient D and the solubility S of the gas in the polymer, according to (14)

$$Q = -DS\,(p_1 - p_2)/l$$

if $(p_1 - p_2)$ is the pressure difference across a wall of thickness l.

The factor $(p_1 - p_2)$ is comparable to $(V_m - V_t)$ in which the composition of air has been taken into account (Sections 3.6 and 3.7). Since the 'permeability' $P = \bar{f}/\overline{dp}$ we can write

$$P \sim -Q/(p_1 - p_2) = DS/l$$

and also:

$$\frac{P(O_2)}{P(N_2)} = \frac{D(O_2)\,S(O_2)}{D(N_2)\,S(N_2)}$$

In Section 3.6 it was found that the solubilities of atmospheric oxygen and nitrogen in the fat-free phase of dried milk are about equal. Considering the composition of air, this means that the actual solubility ratio $S(O_2)/S(N_2)$ is about four. This latter figure is far from accurate, however, in view of the fact that both solubility values are only rough approximations. In fact, if the actual values were to deviate by only 0.1 ml/100 g, a solubility ratio of seven would be possible. This would at least offer a partial explanation for the high maxima in Fig. 9, in so far as the continuous fat-free solid phase of dried milk particles is comparable to polymers.

The powders contain, however, a dispersed fat phase and the 'permeability' increases with increasing fat content (Fig. 8), indicating that the gas transport through the fat may be faster than through the fat-free phase.

The composition and structure of dried milk particles are far too complex to allow a rigorous treatment in terms of solid state diffusion theory. The above speculations are aimed only at offering a reasonable explanation for the high 'permeability ratio' shown in Fig. 9.

3.9 Tentative model

Based upon the data produced so far, the following phases in the gas penetration into our milk powders can be distinguished. During the first hours of storage, ordinary air penetrates through relatively wide micropores into the most accessible vacuoles. The second phase is characterized by the fact that comparatively more oxygen than nitrogen is taken up. When most of the particles have been almost 'saturated' with oxygen, the third phase starts in which nitrogen transport dominates.

Phase one. The largest pores cannot be expected to have a selective effect upon oxygen and nitrogen, which means that a large part of the gas penetrating during this phase may be air of normal composition. This implies that the 'permeability ratio' would have about unit value at zero time and Fig. 9 shows that this may well be the case.

For a proper measurement of the residual gas volume of fresh powders it is important that the untreated powder samples should not be exposed to air. The sampling procedure described in Section 2.2 meets this requirement.

Phase two. This is the most important phase in our experiment, lasting at least one month. It might be expected that the small micropores of molecular dimensions, as described by Berlin et al. (6, 7), can play an important role in this phase. Flow through such pores is stated to be a function of (among others) the diameters of the diffusing molecules. Since oxygen and nitrogen are about equal in this respect and yet their 'permeability ratio' is well above one, it seems unlikely that such micropores contribute considerably to the gas transport during this phase. Moreover the low $\bar{f}$ values suggest that diffusion rather than flow is predominant. If we simply apply Fick's first law to our dried skim milk we can estimate the order of magnitude of the 'diffusion coefficient'. For this calculation we used our $\bar{f}$ values, a particle surface area of 4000 cm^2/g (Buma, 10) and a concentration difference of 0.2 ml/100 g across an 'average wall' of 5 μm thickness. Based upon these approximations it is found that after the first days of storage the order of magnitude of the 'diffusion coefficients' lies between 10^{-12} and 10^{-13} cm^2/sec.

Towards the end of phase two, the residual oxygen volumes approach their V_m values while the nitrogen volumes are still far from equilibrium. Inaccuracies in the calculation of V_m (O_2) will be magnified in the parameter $\overline{dp}$ and simultaneously an accurate graphical measurement of the oxygen flux becomes increasingly difficult. Therefore, the 'permeability ratio' found after prolonged storage must be considered with caution. Nevertheless, these ratios show a marked tendency to decrease, in some cases already after a few days (D_{25} and D_{10}). This is not surprising. It should be realized that when the more accessible vacuoles have already been filled with oxygen, nitrogen is still penetrating into these vacuoles. In other words, the bulk of the oxygen flux at time t = 25 days for instance takes place through relatively thicker walls than does the bulk of the nitrogen flux at the same time. This 'lagging behind' of nitrogen will eventually cause the curves of Fig. 9 to descend towards subunit values.

Phase three. During this last phase it is mainly nitrogen which penetrates the powders, quite probably by diffusion. Fig. 7 shows that the nitrogen flux $\bar{f}$ reaches a low level while $\overline{dp}$ is still large. Therefore this phase covers a long time, probably more than one year for most of our powders.

Samenvatting

J. G. P. Verhey, *Het binnendringen van lucht in melkpoeder*

Melkpoeders met verschillende vetgehaltes, verkregen door middel van wiel- en drukverstuiving, werden bij kamertemperatuur bewaard. Penetratiecurven van zuurstof en stikstof werden verkregen door middel van regelmatige bepaling van de volumina rest-gas en zuurstof. De evenwichts volumina van beide gassen werden voor elk poeder berekend en de penetratiesnelheid van de gassen werd gerelateerd aan de concentratieverschillen.

Het gasvolume in vers wielpoeder bleek ongeveer half zo groot als het vacuolenvolume, terwijl de vacuolen van drukpoederdeeltjes slechts ongeveer 20% lucht bevatten. Zuurstof

drong sneller in het poeder dan stikstof en de aanwezigheid van vet verhoogde de transportsnelheden. Met inachtneming van de grote variatie in de struktuur van de individuele deeltjes konden de resultaten kwalitatief verklaard worden.

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Vacuole formation in spray powder particles
1. Air incorporation and bubble expansion

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Abstract

The development of vacuoles during the spray drying of skim milk particles was studied, primarily by measuring the volumes of air and vacuoles present in powders produced under various processing conditions.

The results indicate that a certain degree of foaming occurs in the atomizer, yielding spray droplets that contain air bubbles. Severe foaming and high air and vacuole contents of the product were found to result from disc atomization as compared to pressure atomization. Air incorporation on the disc was promoted by low viscosities of the liquid but not by a low solids content as such.

The final vacuole volume of a powder was always found to be higher than the air volume measured under standard conditions and the relative difference was increased when more severe drying conditions existed. It is assumed that drying droplets develop a crust of increasing strength that offers increasing resistance against shrinkage ('case hardening'), so that the air bubbles are forced to expand when the last of the water is removed from the droplet's centre.

The results lend strong support to a hypothesis of vacuole formation comprising two stages, viz air incorporation into the liquid during droplet formation and expansion of air bubbles due to case hardening during drying.

1 Introduction

The presence of vacuoles in spray-dried milk particles has usually been explained as being the result of air incorporation into the liquid during atomization (1, 2, 3, 4). This view is reflected in such names as 'air cells', 'enclosed gas' or 'entrapped air'.

On the other hand it has been suggested (5, 6) that vacuoles might develop without air incorporation. The rapid evaporation during spray drying would cause the surface of the droplets to solidify ('case hardening', 'crust formation') and if this crust were rigid enough, the removal of water from the interior of the particle would leave a vacuole, probably by means of some boiling process. The existence of steep concentration gradients near the surface of the drying droplets has indeed been shown by calculations and by flavour retention studies (7, 8).

In a previous paper (9) we reported that fresh milk powders do contain certain air volumes, but these volumes (measured at 20°C and 1 kg/cm^2) were considerably smaller than the corresponding vacuole volumes. These observations might fit into either of the above theories and further studies were undertaken which will be reported in part in this paper.

In the meantime, Antonson (10) suggested that two kinds of vacuoles exist, viz those consisting of air bubbles originating from spraying, and others that develop during drying and which may be air-free.

This view offers a convenient explanation of our observation mentioned above, but it is difficult to imagine why air-free vacuoles would develop in a drying droplet that already contains air bubbles. Expansion of existing air bubbles would seem more logical.

2 Methods

2.1 Production of powders

The standard conditions for producing dried skim milk include pasteurization of the skim milk (14 s at 72°C) and concentration to about 45% total solids in a batch evaporator, operating at temperatures below 45°C. The concentrates are then fed into the atomizer at 30–35°C and care is taken to avoid any air incorporation into the liquids prior to atomization. The inlet and outlet temperatures of the drying air are 140° and 90°C, respectively. Both centrifugal disc and pressure nozzle atomizers, as depicted in a diagram of the drying plant (9) are used.

Several deviations from these standard conditions will be specified when describing the different experiments.

2.2 Analysis of powders and concentrates

Residual gas volumes and vacuole volumes of freshly prepared powders were measured according to the methods published earlier (9, 11). The volume of air dissolved in concentrated skim milk was measured by means of a modification of the method for the determination of the residual gas volume in powders. This modification consists of drawing a 200 ml liquid sample into a sample flask which has been pretreated with carbon dioxide.

2.3 *Microscopy*

Throughout this work we checked our powders by microscopical observation. Usually a small sample of powder was dispersed in a drop of paraffin oil and observed with normal lighting (illumination from below).

2.4 *Viscosity measurements*

In the course of this work data were needed on the viscosity of concentrated skim milk under the conditions of atomization. Non-Newtonian behaviour of such concentrates was sometimes observed by measuring apparent viscosity under different conditions of flow. We used a 'Rheo-viskometer' according to Hoeppler. In this apparatus the sample is contained in a cylindrical tube together with a glass ball that has a slightly smaller diameter than the tube. A steel rod connects the ball to a balance arm that can be loaded with different weights. Multiplication of this weight by a tube constant and by the time the ball takes to sink 30 mm down yields the apparent viscosity (η' = stress divided by shear rate).

Approximate values for the maximum shear rate during each measurement were obtained from the velocity of the ball during the measurement divided

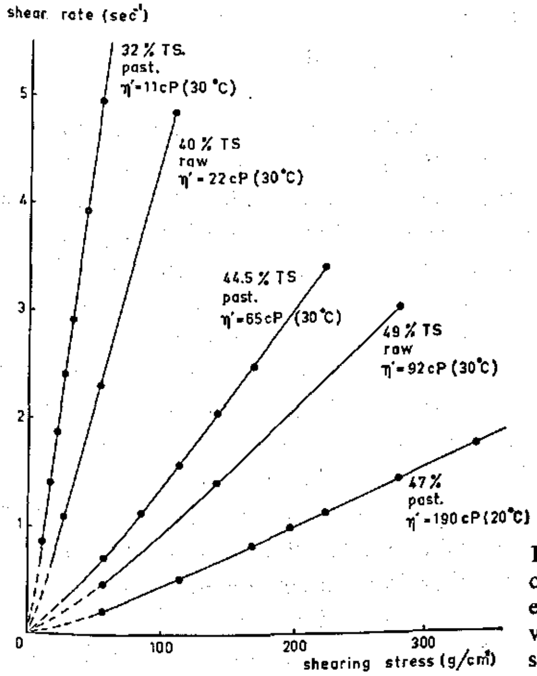

Fig. 1. Viscosity relationships of concentrated skim milk (past = preheated 14 s at 72°C; η' = apparent viscosity value measured at highest shear rate).

by the average play between ball and tube. Multiplication of the shear rate by the corresponding value of η' gave the shearing stress.

Such data calculated for various skim milks are shown in Fig. 1. Apparent viscosities as obtained at the highest shear rates employed are stated in the figure. It will be noted that these liquids behave in an almost Newtonian manner at higher shearing stresses, and the apparent viscosity measured under such conditions is therefore a suitable measure of the viscosity of the liquid in the atomizer, where even higher shearing stresses may well occur.

On the other hand non-Newtonian behaviour is observed at low shear rates and yield values may even exist. This fact should be considered in relation to phenomena such as creaming in concentrated milk.

3 Results and discussion

3.1 The origin of the entrapped air

When residual gas volumes were determined in the experiments described below, the oxygen volumes were also measured. It was found in all cases that the residual gas in fresh powder samples contained about 21% oxygen. We shall therefore use the term residual air volume when referring to freshly dried milk.

In agreement with previous observations (9) each powder analysed in these studies was found to contain residual air. We have to find out during which stage of the drying process this air enters the product.

3.1.1 The feed liquid. Of course the first possible source of air is the concentrated milk itself. Large volumes of air and of other gases can be incorporated in this liquid, which is demonstrated, for example, by the different foam drying techniques. On the other hand it must be noted that the evaporation process is an extremely effective de-aeration procedure, which will certainly yield an air-free product.

In all of the experiments described below, the concentrate was handled carefully in such a way that any foaming, pouring or excessive motion was avoided. We measured the air volume (Section 2.1.) in a skim milk concentrate (45% total solids) immediately after production and we found values of 0.0 ml/200 g liquid. After transferring the liquid to the feed tank no air was detectable either. Samples were also taken at the end of the feed line at the location of the disc atomizer and here we found about 0.1 ml air in 200 g concentrate. This may be caused by the presence of air in a horizontal part of the feed line.

When concentrated milk was kept standing in an open vessel at room temperature with gentle stirring, it took up some air at a very low rate.

It was concluded that in our experiments the concentrated milk makes only a negligible contribution to the air that is found in the powder.

3.1.2 The drying particles. It can hardly be imagined that air would penetrate into drying droplets countercurrent to the flow of water and water vapour. We have to consider, however, the possibility of air uptake in the last stages of drying, when the evaporation is coming to an end.

It was concluded previously (9) that air penetration into powder particles stored at room temperature proceeds so slowly that this process can hardly contribute to the residual air volume of fresh powder. In our present experiments the powders had a higher temperature before sampling. We therefore measured the air uptake of freshly dried skim milk during three hours storage at +60°C, +25°C and —25°C, which yielded about 2, 1.5 and 4 ml/100 g, respectively.

Evidently the air penetration into the warm powder before it is collected in a carbon dioxide atmosphere (5–10 s after atomization) cannot contribute significantly to the air volumes measured.

3.1.3 The spraying process. The remaining possible source of air is the spraying process. This can be divided into the flow of liquid inside and, subsequently, outside the atomizer. It will be shown in the next paper (12) that the air is introduced into the product by a foaming process prior to the actual atomization.

3.2 The inlet temperature of the drying air

It is logical to assume that the air bubbles introduced into the feed liquid during spraying constitute a basis for the vacuoles in the final particles. We know that the vacuole volume is larger than the residual air volume of a powder (9).

As a first approach to the study of the relationships between these two volumes we varied the vacuole volume while keeping the spraying process constant. This can easily be done since it is known in practice (e.g. 13) that powders produced either by disc or by pressure atomization show a decrease in packing density as the temperature of the drying air is raised. This effect is primarily explained as being the result of an increasing vacuole volume (14, 15).

Fig. 2 shows the results of one of the experiments designed for this purpose. The inlet temperature of the drying air was varied and other process conditions were kept constant, except the outlet air temperature and the moisture content of the powder because these parameters are directly linked to the variable.

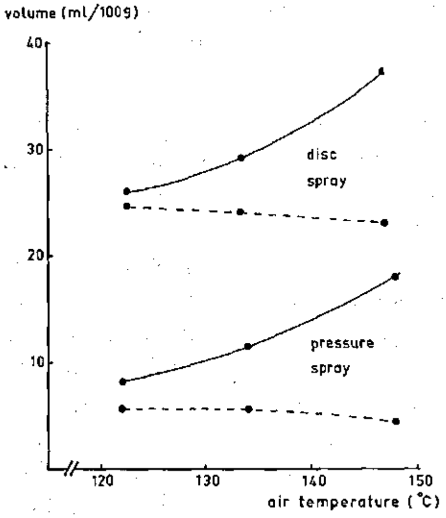

Fig. 2. The volumes of air (----) and of vacuoles (——) in skim milk powders prepared at different inlet temperatures of the drying air.

The figure shows the usual difference between both atomization systems as well as the familiar effect of the inlet air temperature upon the vacuole volume. For each atomization system a certain air volume is found which appears to have no relation to the inlet air temperature, which is in line with the conclusion of the previous section. Upon these observations we based our hypothesis of vacuole formation outlined in the introduction. The increasing vacuole volumes of Fig. 2 are explained as follows.

Higher inlet air temperatures will cause increased evaporation rates, resulting in steeper concentration gradients near the droplet's surface. This condition accelerates the development of a high viscosity surface layer and, eventually, of a rigid crust. Hence, more water will be present inside the droplet when the surface can shrink no more. The shrinkage associated with the evaporation of this larger volume of water will then force the air bubbles to expand more, yielding larger vacuoles. In short: high air temperatures promote case hardening and bubble expansion.

The data of Fig. 2 are also suitable for showing that thermal expansion of the air bubbles can by no means explain the difference between the volumes of vacuoles and of residual air. Neither the cooling of hot air introduced into the liquid nor the heating of relatively cold air bubbles would result in the relationship shown in Fig. 2. If, for example, 5 ml air would be heated at constant pressure from 40°C towards either 120° or 150°C, volumes of 6.3 and 6.7 ml, respectively, would result. Thermal expansion or shrinkage of air bubbles may certainly occur, but these effects are far too small to explain our present results.

3.3 Particle size and particle density

In subsequent experiments we tried to influence the air incorporation process by changing certain properties of the feed liquid such as viscosity and water content. As a side effect changes in the particle size distribution of the powder may then occur. This complicates the correct interpretation of the results if the air and vacuole volume of individual particles are related to particle size.

To investigate the relationship between particle size and particle density (vacuole volume) several skim milk powders produced in our drier were fractionated by sieving and the vacuole volume of each fraction was measured. Representative results are shown in Table 1. In pressure spray powders, smaller particles are denser than larger ones and the differences are considerable. The same observation was reported by Pyne (16) and by Buma (17). In centrifugal spray powders the relative differences are far smaller and no evident relationship is found. Residual air volumes were not measured in the sieve fractions because these volumes might change unpredictably during the sieving operation which took about one day (9).

It is concluded from Table 1 that disc atomization is to be preferred in the study of the air incorporation process, since in this case moderate variations in the size distribution may probably be ignored. Further work will of course be needed for pressure atomization.

Table 1. Vacuole volumes (ml/100 g) of sieve fractions of some skim milk powders.

	Pressure nozzle		Centrifugal disc	
	Sample 1	Sample 2	Sample 3	Sample 4
whole sample	26	11	42	32
> 90 μm	18*	18	35	21
90–71 μm	30	12	43	27
71–56 μm	34	14	44	31
56–45 μm	33	13	44	35
45–32 μm	18	9	45	35
< 32 μm	7	3	40	31

* This fraction contained many broken particles.

3.4 The volumes of residual air and of vacuoles

The process of air incorporation in the feed liquid is a surface phenomenon that may well be related to the foaming properties of the liquid, such as surface tension and foam stability. The well known practical experience (18) that whole milk powders usually exhibit a smaller vacuole volume than do skim milk powders may be explained by the better foaming properties of skim milk and its concentrates (19). We observed extremely high vacuole volumes when spray drying sodium caseinate solutions, which are easily whipped into stable foams. Somewhat denser powders were obtained from solutions of a household detergent, possibly because such liquids have a poor foam stability as compared to protein solutions.

On the other hand, spray powders prepared from poorly foaming liquids, such as buttermilk, coffee extract and solutions of lactose and maltodextrin, contain small vacuole volumes (unless gas is introduced purposely as is the case with most spray-dried instant coffee).

More details concerning the nature of the foaming process will follow in subsequent communications.

3.4.1 Degree of concentration. The vacuole volume of disc spray-dried milk powders is closely related to the solids content of the feed liquid (18). We utilized this experience for varying the air incorporation without altering other drying conditions.

Four batches from one lot of skim milk were concentrated to 35, 40, 45 and 50% total solids and spray-dried in the usual way (Section 2.1) by disc atomization. During each drying run the apparent viscosity (Section 2.2) of a feed liquid sample was measured at the feed temperature. Since the feed rate was kept constant, as well as the inlet temperature of the drying air (138°C), the outlet air temperature and the moisture content of the powders varied somewhat.

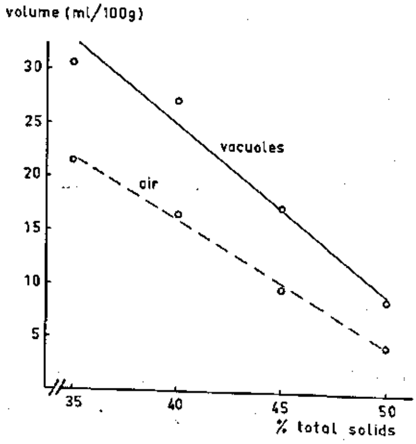

Fig. 3. The volumes of air and vacuoles in centrifugal spray skim milk powder as a function of the solids content of the feed liquid.

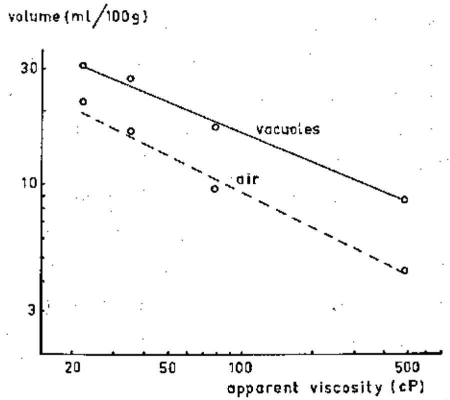

Fig. 4. The volumes of air and vacuoles i disc spray skim milk powder as a functio of the apparent viscosity of the feed liqui (data of Fig. 3).

The residual air and vacuole volumes of the four powders are shown in Fig. 3. Further concentration yields a denser powder with less air. Now that the inle air temperature is kept constant, the vacuole volume appears to be fairly closely related to the residual air volume (cf. Fig. 2). This relation is not a simple linear one since the difference between both volumes is not constant and neither is their ratio.

However, an interpretation of the present results can hardly be given since the variable is directly linked to many other relevant parameters, such as viscosity, diffusion coefficients, interfacial tension, vapour pressure and degree of shrinkage during drying. Therefore further experiments were carried out in which either the solids content or the apparent viscosity was kept constant.

3.4.2 Apparent viscosity. In one experiment we subjected three lots of skim milk to different heat treatments prior to condensation to 45% total solids (15 min at 72°C, 30 min at 72°C and 30 min at 85°C), yielding apparent viscosities

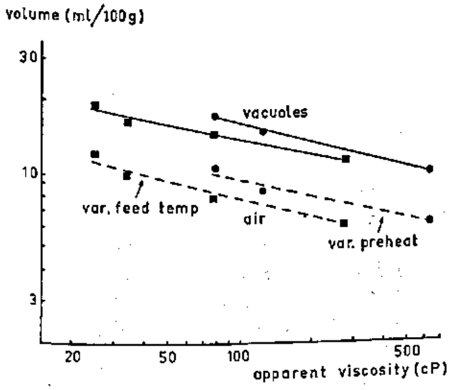

Fig. 5. The relationship between the apparent viscosity of condensed skim milk (45% total solids) and the volumes of air and vacuoles in the powders made from it. Viscosity variations were obtained by varying either the feed temperature (squares) or the preheat treatments (dots).

of 80, 125 and 620 cP, respectively, at the usual feed temperature of 35°C. In another experiment the feed temperature of a skim milk concentrate (44.5% total solids) was varied (53, 47, 31 and 13°C), which caused the apparent viscosity to range from 25 to 275 cP. All apparent viscosities were measured during each production run at temperatures equal to the feed temperature.

In a logarithmic plot the results can be reasonably represented by straight lines (Fig. 5). Similarly, the data of Fig. 3 are reproduced in Fig. 4 as a function of the viscosities measured in that experiment. Although the slope of the lines in Fig. 5 is less steep than of those in Fig. 4, it appears that a considerable part of the 'solids effect' must be attributed to viscosity. Further discussion will be given below.

3.4.3 Water content. To study the effect of water content as such, a series of concentrated (skim) milks with different water contents but equal viscosities is needed. Again, this was done in two different ways as can be seen in Tables 2 and 3. In both cases different heat treatments were applied before concen-

Table 2. The production of condensed skim milks with varying solids content but with approximately equal viscosities at the temperature of atomization.

	Batch number			
	1	2	3	4
Preheat treatment	30 min 90°C	30 min 90°C	—	—
Thickening agent added (%)	0.15	0.07	0.02	—
Solids content (%)	34	38	44	49
Feed temperature (°C)	20	20	22	30
Apparent viscosity (cP)	65	66	72	69

Table 3. As for Table 2, but without thickening agent.

	Batch number			
	5	6	7	8
Preheat treatment	30 min 90°C	30 min 90°C	—	—
Total solids after condensing (%)	40.5	40.5	49	49
Ageing	1 day	1 day	1 h	none
Total solids during spraying (%)	35.5	40.5	45	49
Feed temperature (°C)	25	44	40	50
Apparent viscosity (cP)	33	32	33	30–35

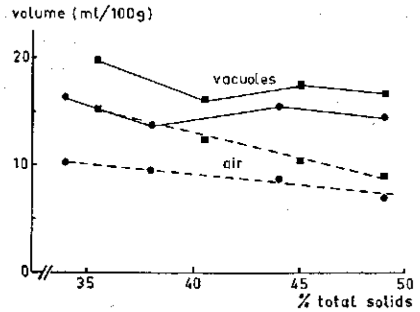

Fig. 6. The concentration of condensed skim milk versus the volumes of air and vacuoles in the powders made from it. Dots: $\eta' \approx 70$ cP (Table 2); squares: $\eta' \approx 30$ cP (Table 3).

tration. In the first experiment efforts were made to maintain the feed temperature at a fairly constant level and therefore a thickening agent was used namely carboxymethyl cellulose. The latter addition was avoided in the second experiment and, after ageing the low solids concentrates, the feed temperatures could still be kept within reasonable limits.

The different viscosity levels in both experiments are reflected by the results (Fig. 6), and it is also observed that the air and vacuole volumes still decrease with increasing solids content. However, it is not satisfactory to express the air volumes as ml/100 g powder only. The volume of feed liquid yielding 100 g powder varies with its solids content and the air is supposed to be incorporated in this liquid. Therefore we expressed the air volumes in Fig. 6 (little variation in η') and also those in Fig. 3 (large variation in η') as ml/100 ml feed liquid and these are plotted in Fig. 7. It may now be concluded that the water content of the feed liquid as such has little or no effect upon the process of air incorporation.

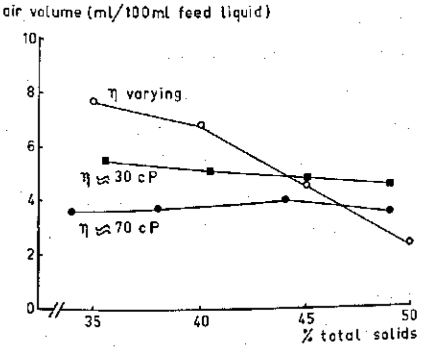

Fig. 7. Air content of freshly atomized droplets plotted against the initial solids content. Data from Fig. 3 (varying viscosity) and from Fig. 6 (constant viscosity).

3.4.4 Air incorporation related to the properties of the feed liquid. In Fig. 8 the residual air volumes are expressed as ml/100 ml feed liquid for the experiments in which viscosity was varied. Evidently, it does make any difference

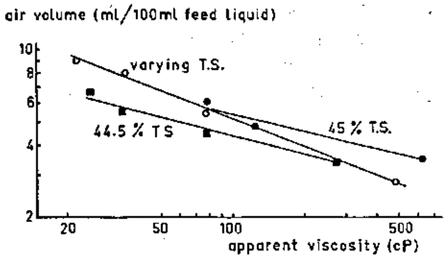

Fig. 8. Air content of freshly atomized droplets plotted against the apparent viscosity of the feed liquid. Data from Fig. 3 (varying total solids) and from Fig. 5 (constant total solids) are reproduced.

whether or not the total solids content is constant. It is concluded that the apparent viscosity as such is not the only property of the liquid that governs air incorporation, although it accounts for the greater part of the variation between samples. Possibly the water content of the feed liquid exerts an additional influence via its relation to surface properties.

It must be realized, of course, that the validity of these relationships is limited to disc spray drying of concentrated skim milk.

3.5 Expansion of air bubbles

Firstly, a general quantitative aspect of air bubble expansion needs to be mentioned. The true volume (computed from the true density) of 100 g skim milk powder is about 68 ml, and it results from drying a volume of liquid varying from some 240 ml (35 % solids) to 160 ml (50 % solids). Total shrinkage varies, therefore, from some 170 to 90 ml/100 g powder. The contribution of air bubble expansion to this volume change amounts to no more than roughly 5 %. By far most of the total shrinkage is brought about by actual shrinkage of the droplet, or in other words, by reduction of the droplet's diameter.

The degree of expansion of the air volume may be expressed by the average pressure in the vacuoles (ratio of air to vacuole volume), if we neglect the small amount of air that may have dissolved in the fresh particle material (9). Other expressions were calculated as well, such as the absolute volume increment of the air, and this same increment relative to the original air volume or to the total shrinkage of the liquid, etc. However, the average pressure appeared most suitable. The values obtained experimentally for this parameter are presented in Fig. 9, 10 and 11.

Fig. 9 shows that in particular the inlet temperature of the drying air governs bubble expansion. It should be remembered that in this experiment no changes occurred either in the properties of the feed liquid or in the residual air volumes. Apparently the severity of the drying conditions and thus the intensity of case hardening is of great importance.

Fig. 11 demonstrates that increasing expansion occurs at higher solids content

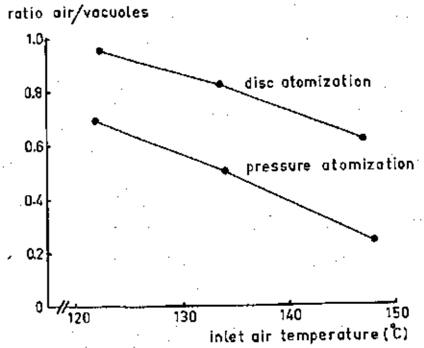

Fig. 9. The ratio of air to vacuole volumes derived from the data of Fig. 2.

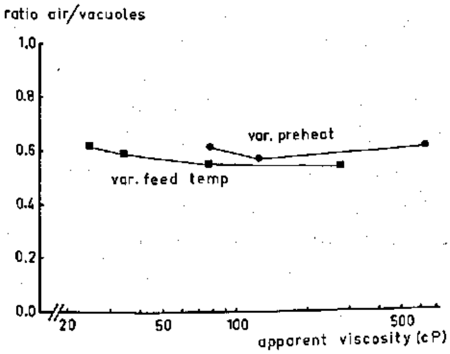

Fig. 10. Ratio of air to vacuole volume as a function of the apparent viscosity of the feed liquid. Data from Fig. 5 (constant total solids).

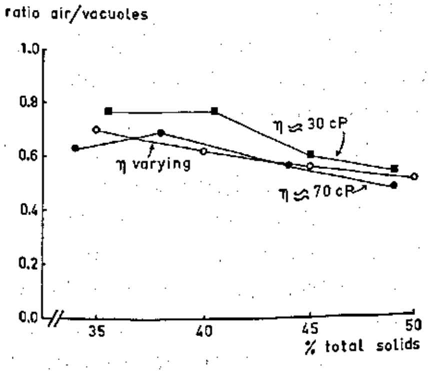

Fig. 11. Ratio of air to vacuole volumes as a function of feed liquid concentration. Data from Fig. 3 (varying viscosity) and from Fig. 6 (constant viscosity).

of the feed liquid. Again this is related to drying conditions and case hardening. With respect to bubble expansion the total solids content of the feed liquid has two opposite effects, viz degree of shrinkage and intensity of case hardening. It was mentioned above that the total shrinkage during drying varied considerably in our experiments. It might be expected that extensive shrinkage (low solids content) leads to increased bubble expansion, but this is exactly opposite to the observations.

On the other hand a low solids content implies that a relatively large amount of water evaporates prior to the actual case hardening. This evaporation reduces the severity of the drying conditions (falling temperature and rising humidity of the drying air), and thus the actual case hardening takes place under milder conditions, leading to smaller bubble expansion at lower solids content of the feed liquid. This effect is assumed to account for the trend observed in Fig. 11.

The air content of the initial droplet (Fig. 6 and 7) is inversely related to its liquid content and shrinkage. This effect is also in line with the results, but it is relatively small.

The effect of apparent viscosity upon bubble expansion (Fig. 10) is so small that it will not be discussed.

The existence of a close relationship between severe drying conditions and case hardening is indicated by yet another series of experiments. These were carried out some years ago before we developed the method for measuring residual air volumes. A considerable increase in vacuole volumes was observed when the feed rate was decreased. Of course the outlet air temperature rose and more severe conditions of drying existed at lower feed rates. Two graphs given by King (15) also demonstrate that large capacities (feed rates) lead to higher powder densities.

The crust developing in a drying droplet can also be observed microscopically. Droplets originating from different atomizers and travelling through air of various temperatures, were caught on a slide glass covered with a layer of paraffin oil. We used concentrated skim milk (35 % total solids), a simple two-fluid atomizer made from glass tubing and a cocurrent flow of drying air at about 70°C. The samples were taken about 20 cm from the atomizer. Fig. 12 shows some typical particles photographed in such samples. In most cases the crust shows a regular dent pattern, but probably this stage is preceded by a globular crust that is observed as well. Correct sampling of droplets during the normal spray drying operation appeared unfeasible. Therefore the value of these photographs should not be overestimated. They do show, however, a tendency towards crust formation and uneven shrinkage (surface folds) even though the drying conditions were quite mild.

3.6 Pressure atomization

The preceding sections mainly deal with centrifugal disc atomization, for the reason given in Section 3.3. If our hypothesis on vacuole formation is correct,

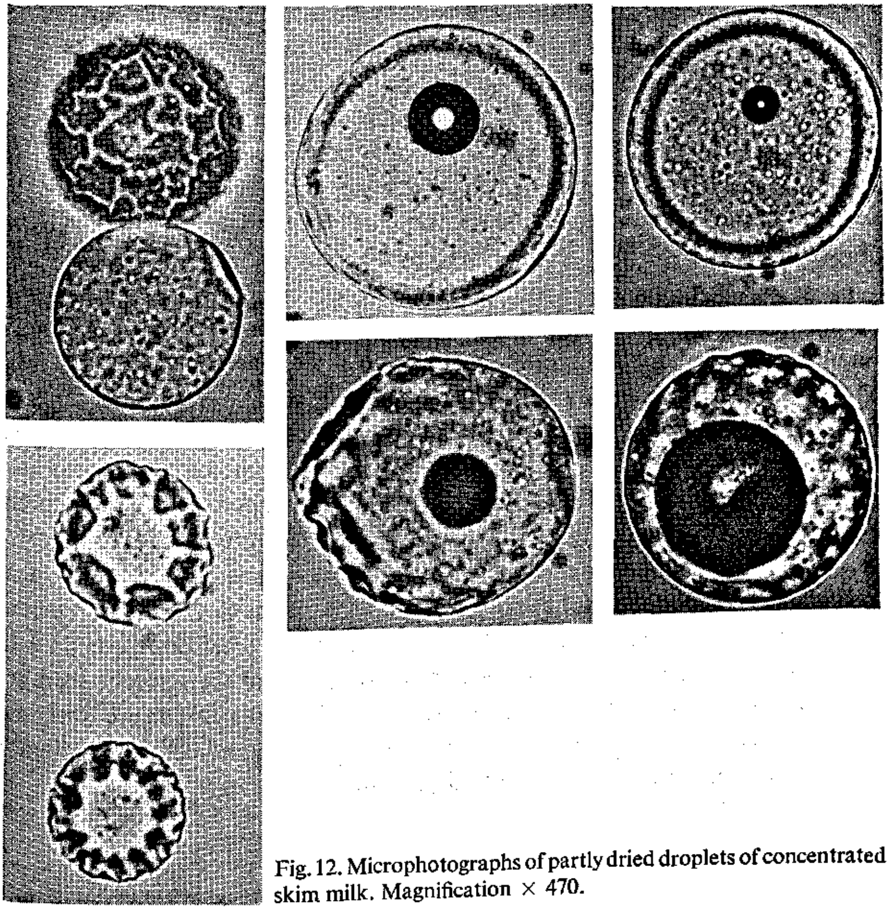

Fig. 12. Microphotographs of partly dried droplets of concentrated skim milk. Magnification × 470.

it should apply to pressure spray drying as well. Although we shall return to the different atomization systems in a future communication, a few remarks will be made at this stage, partly based upon the data of Fig. 2 and upon those given previously (9).

The main difference between disc and pressure atomization lies in the process of air incorporation. Not only is the vacuole volume in pressure spray powder far smaller than the corresponding volume in disc spray powder (18), but the average number of vacuoles in one particle is even more different, as can be observed microscopically. Many pressure spray particles are free from vacuoles, whereas disc spray particles usually contain some ten to a hundred vacuoles.

It seems reasonable to state that the 'foam-generating action' of a pressure nozzle is relatively weak, yielding a rather coarse air dispersion of low air content. This difference from disc atomizers may be attributed to the far smaller air/liquid interface and to the more controlled flow in a pressure nozzle.

Concerning air bubble expansion it is noted that the contribution of this factor to the total volume reduction during drying is remarkably equal when corresponding disc and pressure spray powders are compared, either in Fig. 2 or in previous results (9). Apparently the differences in the air volumes and in the pressures resulting after expansion are of minor importance and the conclusion drawn in Section 3.2 may also apply to pressure atomization.

From unpublished older experimental data it was concluded that the relation between the vacuole volume and the concentration of the feed liquid, that is a familiar feature of disc atomization, is virtually absent in pressure spray drying. This observation is certainly not new (18). It is explained partly by the absence of air bubbles in many droplets because no bubble expansion (nor bubble formation) occurs there anyway. Furthermore, the volume of air incorporated during pressure atomization may be less dependent upon the solids content and viscosity of the feed liquid than in the case of disc atomization.

The process of case hardening in pressure spray droplets may be complicated by the fact that the flow of the spray and the drying air is of the countercurrent type in our dryer (9), whereas in disc atomization the conditions are close to cocurrent flow. It may be imagined that countercurrent flow results in more severe drying conditions during the early stages of drying. In fact we observed a slight decrease of the vacuole volumes of pressure spray powders when a swirling motion was imparted to the drying air.

4 Conclusion

The work described in this paper was based upon the hypothesis that vacuole formation consists of air incorporation in the liquid during spraying, followed by expansion of this air due to case hardening in the drying and shrinking droplets. This hypothesis appeared quite suitable for explaining our present results, but since its validity has not yet been sufficiently proven, we shall formulate further conclusions in our next communication (12).

Samenvatting

J. G. P. Verhey, *Vakuolenvorming in verstuivingspoederdeeltjes. 1. Luchtinslag en uitzetting van luchtbellen*

De vorming van vakuolen in deeltjes mager verstuivingsmelkpoeder werd bestudeerd en wel voornamelijk door meting van de lucht- en vakuolenvolumina in poeders die onder verschillende omstandigheden waren bereid. De resultaten wijzen op een zekere mate van schuimvorming

tijdens het vernevelen waardoor druppels ontstaan met luchtbellen erin. Wielverstuiving gaat gepaard met intensievere schuiming en hogere lucht- en vakuolengehalten in het produkt dan drukverstuiving. Bij wielverstuiving wordt luchtinslag bevorderd door een lage viscositeit van de vloeistof maar niet door een laag droge stofgehalte als zodanig.

Het vakuolenvolume van het poeder bleek altijd groter dan het onder standaardomstandigheden gemeten luchtvolume en het relatieve verschil tussen beide nam toe met toenemende felheid van droging. Verondersteld wordt dat in de drogende druppels een korst van toenemende stevigheid ontstaat, die steeds moeilijker kan krimpen zodat de luchtbellen worden gedwongen om uit te zetten bij het verdampen van het laatste water uit het binnenste van de druppel.

De resultaten ondersteunen een hypothese voor vakuolenvorming die bestaat uit twee stadia, namelijk luchtinslag in de vloeistof bij het verstuiven en uitzetting van deze lucht tengevolge van korstvorming tijdens het drogen.

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Vacuole formation in spray powder particles
2. Location and prevention of air incorporation

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Abstract

We assumed previously that vacuoles result from air incorporation into the liquid to be dried, followed by air bubble expansion. The present paper deals mainly with the first part of this process, viz air incorporation.

Two series of experiments were undertaken. In one series the purpose was to replace the air normally present inside an atomizer by carbon dioxide. This gas was then isolated from the resulting powders instead of the usual air. It was concluded that gas incorporation into the liquid ('foaming') occurs inside the various atomizers.

In the other experiments the atomizers were flushed with steam instead of carbon dioxide. Because of the rapid condensation of the steam bubbles in the drying droplets, vacuole development was apparently inhibited. It could be concluded that the presence of gas bubbles in the drying droplets is an essential requirement for vacuole formation.

Finally, this paper deals with some practical aspects of the production of vacuole-free powders by means of 'air-free' atomization.

1 Introduction

In a previous paper (1) we suggested that vacuoles in spray-dried milk particles originate from air bubbles incorporated during spraying which subsequently expand during drying. A more direct proof of this assumption was considered useful, and it is also desirable to localize this 'foaming process' more precisely within the successive stages of spraying.

For these purposes the air normally present in the atomizers may be replaced by another gas, and tests should be carried out to determine which gas is present in the powder particles. The results of such experiments will be presented in this paper as well as their implications for the hypothesis on vacuole formation given in an earlier paper.

From this model it may be concluded that vacuole-free powders must be obtained when air incorporation during atomization is eliminated. This con-

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clusion will be verified experimentally, and details on 'air-free atomization' and its practical aspects are also described below.

2 Methods

2.1 General

The preparatory methods employed in the present experiments are the same as those described earlier (2) unless stated otherwise. To the analytical procedures (1, 2, 3) the following were added.

2.2 Measurement of the residual CO_2 volume in dried milks

2.2.1 Principle. An air stream transfers the carbon dioxide gas from an acidified solution of the powder to an alkaline solution which is subsequently titrated.

2.2.2 Procedure. An amount of 40 g of freshly prepared powder is quickly weighed in a 500-ml flask containing a magnetic stirring rod. A drop of antifoaming agent is added and the sample is protected from the atmosphere by fitting the bottle with a separatory funnel. Through the funnel 150 ml 96% ethanol (free from CO_2) are introduced; the powder is dispersed by stirring. By the subsequent addition of 200 ml 1.25% hydrochloric acid solution the powder is dissolved and simultaneously the pH of the sample solution is lowered to about 3.

An air flow of 400 ml/min is generated by a water jet pump. The air first passes through two columns of soda lime to remove CO_2, then it bubbles through the sample solution and finally through three washing bottles, each containing 100 ml 0.05 *N* barium hydroxide solution. While the sample is stirred, the air flow is maintained for 30 minutes but in the beginning it is interrupted three times by closing the air inlet of the sample flask. Thus the system is evacuated, which accelerates the removal of the gas from the sample. Finally the amount of CO_2 is measured by titrating the three alkaline solutions according to Dutch standard NEN 3104, and the result is expressed as ml CO_2/100 g powder.

2.2.3 Remarks. The procedure is carried out at room temperature since CO_2 may be formed by chemical reactions when milk products are heated.

Normal powders yielded blank values of about 1 ml/100 g. The titration value obtained from a reference powder included in each experiment was used as a reagent blank.

The recovery of known amounts of CO_2, added to the powder sample in the form of sodium carbonate, was found to very from 100 to 104%.

Duplicate results obtained on experimental powders usually differed by less than 3 ml/100 g.

2.3 Measurement of the packing density of powders

Bulk density or packing density (ϱ_p) was measured with a device that is commonly used in the Dutch milk powder industry. It consists of a vertical cylinder (internal diameter 30 mm) in which one ounce of powder is tapped mechanically one hundred times while a cylindrical weight of 71 g covers the powder column. After tapping, the specific volume is read and its reciprocal is the packing density.

3 Results and discussion

3.1 Atomization in a CO_2 atmosphere

3.1.1 General. To prove the assumption that air is incorporated into the feed liquid while passing through the atomizer, we replaced the air inside the atomizer by CO_2 and measured the residual air and CO_2 volumes in the powders. The choice of this gas was based primarily upon the method for measuring the residual air volume (3). In this method CO_2 is used to aid in removing the external air from the powder sample. Towards the end of the procedure, this gas is removed by alkali, leaving the air behind. If, after atomization in the presence of CO_2, the resulting powder contains both this gas and air, it will still be possible to measure the residual air volume in the usual way. In fact, in most of our experiments only the residual air volume was measured and the reduction of this volume was considered to be due to the incorporation of CO_2. The absolute proof could only be given after we had succeeded in developing a method for measuring the residual CO_2 volume (Section 2.2).

3.1.2 Disc atomization. The arrangement for disc atomization in a CO_2 atmosphere is shown in Fig. 1. Rather large volumes of gas must be blown into the disc to expel the air. Quite probably this is caused by the fact that the rotating disc acts somewhat like a centrifugal air pump.

The relationship between the flow rate of CO_2 and the residual air volume of the powder can be read from Fig. 2. The shape of this curve varied with certain conditions, such as the type of disc and the properties of the feed liquid. Gas flow rates beyond about 50 l/min could not be used because the liquid then

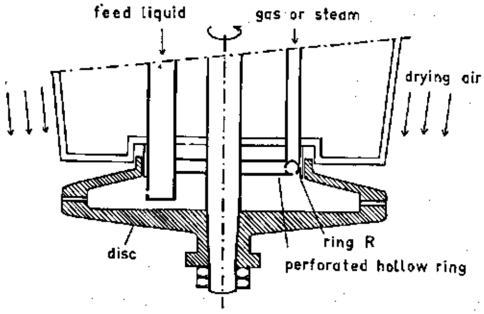

Fig. 1. Sectional diagram of the atomizer disc used in the experiments.

tended to flow over the top of the disc. Fig. 2 suggests that the highest flow rate used is quite effective, although there is no proof that the CO_2 content of the gas inside the disc reaches 100%.

It is important to note that any effect of the gas treatment must be attributed to the presence of CO_2 inside the atomizer disc and, possibly, in the streams of liquid and gas leaving the orifices. However, directly around the disc the drying air is flowing downward at a rate of 35 m^3/min, which is 700 times the highest CO_2 flow used. This will strongly dilute the gas within a few millimetres beyond the orifices.

In a further experiment the presence of CO_2 in the disc was again related to the residual air volume, but also to the volumes of vacuoles and residual CO_2 in the powder. Table 1, reporting this experiment, shows that the gas treatment almost completely removes the air, and that now CO_2 is found in the powder. This shows that gas incorporation has taken place inside the disc (or also immediately outside the orifices) and that it is not the drying air colliding with the spray, which is enclosed in the droplets.

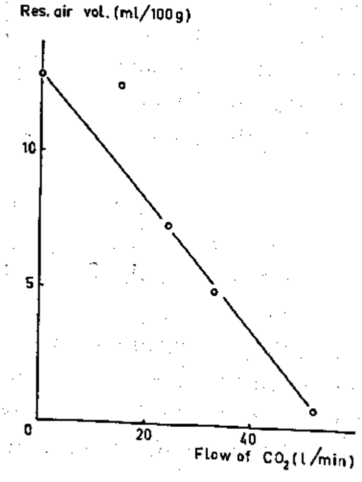

Fig. 2. Residual air volumes of disc-sprayed skim milk powder as a function of the flow of carbon dioxyde into the disc.

Table 1. Vacuole volumes and volumes of residual air and carbon dioxide (1 atm., 20°C) in disc spray-dried skim milk prepared with and without flushing the disc with carbon dioxide gas.

Flow of CO_2 (l/min)	Vacuoles (ml/100 g)	Air (ml/100 g)	CO_2 (ml/100 g)
0	33.0	22.5	0
52	11.3	2.3	11.3

Only 11.3 ml CO_2 was found in the treated powder (Table 1) compared to twice as much air in the reference sample. It can hardly be expected that this difference has originated from the gas uptake in the atomizer. It should rather be supposed that half of the CO_2 volume incorporated originally has been lost subsequently by solution and volatilization. This is not surprising since this gas dissolves very rapidly in aqueous liquids.

We assume that the lower vacuole volume in the treated powder must also be explained by the dissolution of CO_2.

Some of the CO_2 dissolved in the droplets will vaporize during drying, but at a lower rate than water due to its molecular size (4). This increases the amount of gas returning to the vacuoles during evaporation of the last amount of water. Furthermore, some gas will remain dissolved in the solid phase of the particles. So we may understand that the gas volume in this powder is not smaller than the vacuole volume.

It is clear that a complete explanation of the results given in Table 1 is quite difficult and further experiments would be required for that purpose. In view of our purpose, however, we were satisfied with the data obtained.

3.1.3 Two-fluid atomization. Two-fluid atomizers can have widely varying designs. Our limited experience indicates that relatively low-density powders are obtained if the gas stream that atomizes the liquid is mixed with the liquid inside the nozzle. If, however, the actual atomization takes place entirely outside the jet-forming device a denser powder results. This probably follows from the reduced possibilities for air incorporation in the latter system.

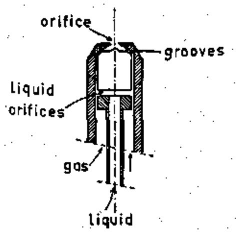

Fig. 3. Schematic sectional diagram of the two-fluid nozzle used in the experiments.

Table 2. Vacuole volumes and volumes of residual air and carbondioxide (1 atm., 20°C) in skim milk powder prepared with a two-fluid nozzle using either air or carbon dioxide as the atomizing agent.

Atomizing gas	Vacuoles (ml/100 g)	Air (ml/100 g)	CO_2 (ml/100 g)
Air	32.0	20.7	0
CO_2	18.2	2.1	16.2

A nozzle that operates satisfactorily in our drier is shown in Fig. 3. It is located in the same position as pressure nozzles (2), so that a countercurrent drying system is obtained. The nozzle was operated with compressed air as well as with CO_2 under identical conditions, yielding the results shown in Table 2. These results are almost identical to those reported in Section 3.1.2.

Again it is concluded that the gas incorporated into the liquid during atomization is not the drying air 'colliding' with the spray, but rather the gas stream used as the atomizing agent. The further comments given in Section 3.1.2 are also valid in this case.

3.1.4 Pressure atomization. High-pressure atomization differs from two-fluid atomization by the absence of an atomizing gas stream. In view of the conclusion of the Section 3.1.3, this fact offers a good explanation for the high density of pressure spray powders. It may even seem puzzling how it is possible that these powders can contain any air and vacuoles. It should be remembered, however, that in this case also the actual atomization does take place in the presence of air. The air-liquid interface is not restricted to the spray cone outside the nozzle, but it advances into the orifice in the form of an extremely thin air core (5). Without this air core, proper atomization does not occur (5, 6). The best way to administer a gas treatment to a pressure nozzle would thus be to lead a small gas stream through the body of the nozzle towards the bottom of the air core, but this could not be realized. The next best solution would be a gas stream approaching the orifice from the opposite direction, but this also posed problems since the spray should not be disturbed.

We ended up with the outfit shown in Fig. 4. The top of the spray cone is flushed from the outside and air may still be present within the cone and the orifice. This device is of course not satisfactory and out of the few experiments that were carried out, one is reported in Table 3. It may seem surprising that rather high gas flow rates are necessary for obtaining a considerable effect. Therefore we placed the nozzle outside the drier and supplied 42 l CO_2/min while spraying water at a normal pressure. By analysing gas samples drawn

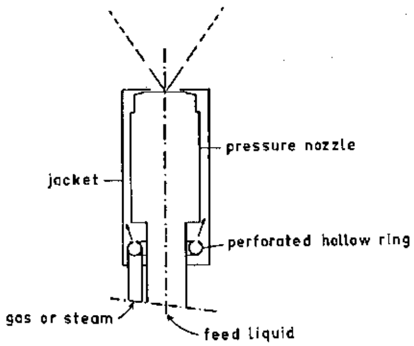

Fig. 4. Diagram of the jacketed pressure nozzle used in the experiments.

from various points around the top of the spray cone, we observed very low CO_2 concentrations ($< 10\%$ v/v) unless the sampling point was not more than a few centimetres away from the gas outlet. Concentrations above 70% of CO_2 were found only in close proximity (<5 mm) to the orifice. This must be a result of the strong draught that is generated by the fast moving droplets.

Thus, in spite of the poor quality of the flushing procedure, these results do indicate that the gas incorporation takes place very close to the atomizer, possibly in the orifice and also at its outer edge.

3.1.5 Discussion. The experimental results obtained above must be applied to the usual situation in which air is present in the atomizer rather than CO_2.

The incorporation of very small air bubbles in a relatively viscous liquid requires an air-liquid interface that is hydrodynamically unstable, and this requires energy. Moreover the time during which unstable conditions prevail must be sufficient to allow the actual formation of an air dispersion or 'foam'. The degree to which these requirements are met in each atomization system may be the cause of the mutual differences with respect to air incorporation. In a subsequent paper this issue will be discussed in more detail.

The above experiments make it clear that air incorporation is not the result

Table 3. The effects of varying flow rates of carbon dioxide (Fig. 4) upon the volumes of vacuoles and residual air in pressure-sprayed skim milk powder.

Flow of CO_2 (l/min)	Vacuoles (ml/100 g)	Air (ml/100 g)
0	11.3	5.7
14	10.7	5.0
28	9.5	4.1
42	9.5	3.5

of the collision of the flow of drying air with the spray. They indicate instead that the air is dispersed before the actual atomization at the moment when the flow of liquid is accelerated in the presence of air. It follows than that the final droplets are not actually formed out of a continuous liquid, but out of a 'microfoam' (7). Some of this dispersed air will be lost during atomization. We found a volumetric air content of 3–8 % in disc spray droplets and roughly 1 % in pressure spray droplets (1). Nevertheless the presence of air bubbles in the liquid may exert some influence upon the size distribution of the spray droplets.

3.2 Atomization in a steam atmosphere

3.2.1 General. In Section 3.1 it was assumed that a considerable volume of CO_2 dissolves in the concentrate during atomization because this would explain the reduction of the volumes of residual gas and vacuoles. Thinking along this line, it would be logical to replace this gas by a condensable vapour such as steam, since steam bubbles might disappear entirely before the formation of a 'crust'. Thus a spray of massive droplets would be obtained and vacuoles would not develop at all.

Actually our research work followed a different sequence. The idea of using steam in the atomizers was born and realised (8) soon after the theory on vacuole development (1) had been postulated. The experiments with CO_2 were performed later with the primary purpose of giving an independent proof of the process of gas incorporation.

Quite recently we were informed about a patent issued in 1955, covering the preparation of high-density powders by means of two-fluid atomization (9). Steam is used in the atomizer instead of the usual compressed air. The results given in the patent seem to be similar to ours (Section 3.2.2), but a satisfactory explanation is lacking. As far as we know the patent has not found practical application. One reason may be that two-fluid atomization is not often applied in spray drying, but probably the main reason lies in the severe heat treatment of the product, occurring in this process (Section 3.2.2).

3.2.2 Two-fluid atomization. Replacing the compressed air in a two-fluid atomizer (Fig. 3) by steam was by far the simplest procedure for air-free atomization. This process turned out to be unsuitable for a heat-sensitive product like milk due to strong overheating by the steam used. Nevertheless these experiments were quite successful in terms of preventing vacuole formation: virtually vacuole-free powders were obtained from condensed milk, skim milk and whey (usually not more than 1 ml vacuoles/100 g). Under normal conditions the same nozzle produces powders containing some 30–40 ml vacuoles/100 g.

It was assumed, of course, that the steam bubbles incorporated during atomization would quickly condense in the relatively cool feed liquid (about 40°C). Therefore we heated a skim milk concentrate to temperatures up to 127°C, measured by means of a thermocouple directly ahead of the atomizer. Again steam instead of air was used for atomization. Although this liquid was well above boiling temperature at the outset of drying, an equally dense powder resulted (about 1 ml vacuoles/100 g). This is a very interesting fact.

In the first place it shows that evaporation lowers the droplet temperature far enough and fast enough to allow the steam bubbles to condense before the droplet surface becomes sufficiently hard or viscous to cause expansion of gas or vapour bubbles.

But it is more important that, even under these favourable conditions, any spontaneous nucleation of vapour bubbles in the drying droplets is apparently inhibited. Quite probably, it is again the temperature depression resulting from evaporation that is responsible.

A further observation during these experiments (also with moderate feed temperatures) was a strongly increased loss of powder dust via the cyclone exhaust. The microscopical appearance of these powders indicated that the whole size distribution was shifted downward. This is not surprising because of the heating of the liquid mentioned above and the subsequent low viscosity of the liquid during atomization.

3.2.3 Disc atomization. The success of air-free disc atomization depends upon details of construction. The aim is to exclude any air from the interior of the disc by flushing this space with steam. First we fitted a perforated ring around the atomizer shaft at the end of a steam inlet pipe (Fig. 1). The ring R was absent at that time. With this arrangement vacuole volumes below about 4 ml/100 g were only obtained when fairly large amounts of steam were used. Therefore the stationary ring R was mounted around the perforated ring to reduce the opening at the top of the disc. Through this opening either air might be drawn into the disc or steam might escape.

A further modification aimed at reducing the steam consumption consisted of closing eight out of the twelve orifices in the disc's periphery. These cylindrical channels had a diameter of 1.5 mm. In this way the efficiency of the process was greatly improved, and thus we arrived at a steam consumption of about 5–7 kg/h yielding very low vacuole volumes.

The steam supply was branched from the air heater steam supply (8 kg/cm^2). Via an insulated $^1/_2$-inch steam pipe it passed through a water separator, a pressure reduction valve and an oil bath. The steam was fed to the atomizer at a pressure of about 15–25 cm Hg above atmospheric pressure and at a temperature around 145°C.

Steam consumption was measured by soaking the disc in a pail of cold water and measuring the temperature and weight increments of the water after a suitable time. The results of these measurements agreed fairly well.

When air-free disc atomization was applied, the vacuole volume of milk powders became almost independent of the drying air temperature (Table 4, items 1–3). Also the degree of concentration no longer affected this parameter. Even a powder made from unconcentrated skim milk had an only slightly lower particle density than a 'regular' powder.

Table 4 shows that very low vacuole volumes are found in the usual spray-dried dairy products when 'air-free' atomization is used. One exception would seem to be sodium caseinate but in this case the feed liquid was certainly not air-free.

The true densities of the non-dairy powders were not measured but microscopical inspection of these powders showed very low vacuole volumes when steam had been used in the disc. Estimates of these vacuole volumes are given

Table 4. Apparent particle density (ϱ_a), packing density (ϱ_p) and vacuole volume (V_v) of powders produced by normal or air-free atomization.

Item	Total solids (%)	Atomizer	ϱ_a (g/cm^3)		ϱ_p (g/cm^3)		V_v (ml/100 g)	
			air*	steam*	air*	steam*	air*	steam*
1. Skim milk, inlet air 120°C	44	disc	—	1.43	—	—	—	1
2. Skim milk, inlet air 140°C	44	disc	—	1.42	—	—	—	2
3. Skim milk, inlet air 160°C	44	disc	—	1.40	—	—	—	4
4. Skim milk	9	disc	—	1.39	—	—	—	4
5. Skim milk	40	pressure	1.26	1.42	0.73	0.85	11	2
6. Skim milk	39	disc	1.12	1.44	0.67	0.81	21	1
7. Whole milk	41	pressure	1.21	1.26	0.74	0.78	5	1
8. Whole milk	50	disc	1.17	1.25	—	0.73	8	1
9. Whey	44	disc	1.21	1.49	0.70	0.83	19	3
10. Sodium caseinate	16	disc	0.61	1.02	—	—	87	20
11. Malto-dextrin	50	disc	1.35	1.48	0.77	0.83	—	<5
12. Whole egg	—	disc	1.18	1.18	0.36	0.64	—	<1
13. Detergent	35	disc	1.90	2.32	0.40	0.83	—	—
14. Coffee extract	25	disc	1.39	1.49	0.24	0.71	—	<5
15. Coffee extract	25	pressure	1.38	1.49	0.55	0.84	—	<5

* Atmosphere in the atomizer.

in the table. The large impact of air-free atomization on the structure of these powders is shown by their bulk densities (ϱ_p).

In the case of malto-dextrin the increase of ϱ_p corresponds fairly well with the ϱ_a values. This relationship is entirely absent in the case of egg powder and it is rather slight in the case of the household detergent and coffee powders. An explanation may be that most or all of the vacuoles in these powders have an open connection with the surrounding air. In microscopical preparations of egg powder particles in paraffin oil it was observed that the oil gradually filled all the vacuoles. Of course such vacuoles will not be detected when ϱ_a is measured with an air comparison pycnometer.

3.2.4 Pressure atomization. The arrangement described in Section 3.1.4 (Fig. 4) was used also for 'air-free' pressure atomization. A suitable steam pressure was 0.5 kg/cm^2, whereby the steam consumption amounted to about 6 kg/h which is roughly the same as in the case of disc atomization. Table 4 shows that the vacuole volumes resulting after the steam treatment in both atomizers are not very different. The effect of steam on pressure atomization is better than the results obtained with CO_2 (Section 3.1.4).

As in the case of air-free disc atomization it was found that air-free pressure atomization renders the vacuole volume of the powder almost independent of the drying air temperature and of the solids content of concentrated skim milk.

3.2.5 Discussion. In this section the process of atomization in a steam atmosphere (air-free atomization) will be discussed in terms of vacuole formation only. Other aspects will be treated in Section 3.3.

The virtual elimination of vacuoles by a steam treatment of the various atomizers satisfactorily confirms the expectation formulated in Section 3.2.1. The magnitude of the required flow of steam was explained primarily by the pumping action exerted by the atomizers, leading to suction of air. The resulting steam current complicates exact localization of the air incorporation process. Nevertheless the evidence justifies the conclusion that air incorporation does not occur beyond a very short distance (e.g. 1–2 mm) from the orifices of the disc or the nozzle.

The application of steam has a secondary effect that need be mentioned. The steam blown into the drier together with the spray will raise the humidity of the drying air by some 4 g/kg air (for disc and pressure spraying). The moisture content of ambient air varies with weather conditions from about 5 to 25 g/kg, but as far as we know, there is no evidence that this large variation has a significant influence on the density of powder particles. However, complete mixing of steam and drying air takes time and thus the relative humidity of the gas phase in the spray zone may be significantly increased if mixing is poor (e.g. two-fluid atomization). This will then reduce the rate of drying and the rapidity of crust formation in the droplets. In this way the presence of steam might even affect vacuole formation if the droplets did contain air bubbles.

The same reasoning holds for the effect of the drying air temperature. This parameter is related only to the degree of expansion of the air bubbles, and it loses its significance when these bubbles are virtually absent. Incidentally, it may be noted that the latter statement is restricted to the process of vacuole formation. The drying air temperature, or more generally the rate of drying, will most probably affect the submicroscopical structure of the particle material (stress during shrinkage, cracks, etc.) as well as the particle surface structure. The more so, possibly, in the absence of vacuoles since the development of vacuoles may reduce the mechanical stress in the drying particles.

The observation that air-free atomization renders the vacuole volume almost independent of the concentration of the feed liquid, merely indicates the effectiveness of the process.

The steam treatment does not remove the air present in the feed liquid. We observed many times that the vacuole volume rose at the end of a batch of powder, obviously because the last feed liquid had taken up some air in the balance tank. Also in the case of item 10 in Table 4 the feed liquid contained air, which was observed microscopically.

Zhilov (10) observed the spontaneous formation of vapour bubbles in drying drops if the air temperature was above 100°C. It follows from our results that this does not apply to our conditions of spray drying, and in fact the conditions in Zhilov's experiments were quite different from normal spray drying (far lower rate of drying).

3.3 Side effects and practical aspects of air-free atomization

3.3.1 Steam quality and steam consumption. When air-free atomization is applied according to Section 3.2 any impurities present in the steam may contaminate the product. For applications in the production of human foods the steam will probably have to meet similar legislative requirements as in the case of UHT processes where direct steam heating is used.

The steam consumption will largely depend upon details of construction, and under optimal conditions it should be very low. In fact, only in the area where air is dispersed into the feed liquid must the air be replaced by steam. The stronger the 'draught' in this area, the more steam will be needed. Our experiences with disc atomization (Section 3.2.3) show that reducing the air flow through the disc improved the effectiveness (vacuole volume) as well as the efficiency (steam consumption) of the process. Several efforts to apply air-free disc atomization in commercial dryers were unsuccessful, quite probably because either the size of the orifices in the disc's periphery or the opening round the shaft was too large. Our results with air-free pressure atomization were easily reproduced with several other driers.

Basically, air-free disc atomization might be feasible without using steam, by eliminating the air-liquid interface responsible for air incorporation. This could be tried, for instance, by designing a disc that is entirely filled with the feed liquid during operation. The development of such a disc might be rather interesting.

3.3.2 Evaporative capacity. Introducing steam into the drying air of a spray drier reduces the evaporative capacity of the drier, even if dry steam is used, because it raises the humidity of the air. However, it was observed several times that the steam treatment resulted in a lower moisture content of the powder. This may be due to the reduced particle size (Section 3.3.4).

When the moisture content of the fresh drying air (varying with weather conditions from about 5 to 25 g/kg) increases by 1 g/kg, the evaporative capacity of a drier is lowered theoretically by about 0.6 %. This can be concluded from psychrometric charts by keeping other conditions constant, such as the air temperatures before and after heating and the relative humidity of the exhaust air. In our experiments the steam consumption amounted to some 4 g/kg air, so that the evaporative capacity was reduced by less than 3 %. It is to be expected that in large-scale operation relatively less steam will be needed, and therefore the evaporative capacity of a drier may not change noticeably.

3.3.3 Temperature effects. Heating of the liquid due to the steam treatment may have several effects that may or may not be favourable. In two-fluid atomization (Section 3.2.2) we found that the steam treatment rendered the powder almost insoluble and particle size was strongly reduced.

More subtle observation was needed for tracing temperature effects in air-free disc and pressure atomization. We knew from previous experiments that the phosphatase activity of concentrated raw milk was not strongly reduced by spray drying under normal conditions. Therefore the experiment reported in Table 5 was carried out. Concentrated raw skim milk was spray-dried under standard conditions with or without the steam treatment at the atomizer. Just before atomization the temperature of the feed liquid was raised either to 40 or 60°C by means of small tubular heat exchangers located directly outside the drying chamber. All phosphatase activities were measured according to Sanders and Sager (Netherlands Standard NEN 3142) in suitable dilutions and expressed as μg phenol/ml skim milk.

Table 5. Some properties of skim milk powders as affected by the stream streatment of the atomizer (air-free atomization).

	Disc atomizer				Nozzle atomizer			
	40°C		60°C		40°C		60°C	
	ns	s	ns	s	ns	s	ns	s
Sample number	1	2	3	4	5	6	7	8
Vacuoles (ml/100 g)	34	2	42	2	5	2	6	1
Phosphatase (μg/ml)	1100	6	1000	10	760	760	740	740
WPN index	7.8	7.3	8.2	7.5	7.9	7.8	8.0	7.5
Sieve fractions (% g/g)								
>71 μm	5	—	—	—	—	—	—	—
45–71 μm	45	5	30	5	45	20	30	10
32–45 μm	20	25	25	25	25	25	25	30
<32 μm	30	70	45	70	30	55	45	60

ns = no steam used; s = steam used.

The results show a striking difference between the two atomizers. The heating of the liquid by the steam treatment at the disc is of the order of normal pasteurization. Phosphatase inactivation is almost complete but the WPN index did not decrease appreciably. Considerably finer atomization is indicated by the sieve analysis. (Microscopical observation of the sieve fractions revealed no important differences with regard to agglomeration.)

In the case of air-free pressure atomization apparently no heating of the liquid occurred but yet the size distribution of the powder shifted downward almost as much as in air-free disc atomization. We assume, therefore, that the finer atomization does not only result from the increased temperature of the liquid and the simultaneous viscosity decrease. It seems that the mere presence of steam in the area where atomization occurs, also improves the effectiveness of atomization.

Explaining this observation is not easy. Interfacial tension, flow characteristics, expansion of steam, retarded drying and adsorption of water vapour at the liquid surface, all complicate the scene. But the observation can readily be used, either for obtaining finer atomization or, if this is not desired, for lowering the energy input (disc speed or nozzle pressure). In this connection a more detailed study of the particle size distributions will be useful.

In normal powders, especially pressure spray powders, particle size is related to vacuole volume (1). It can be imagined that air-free atomization does not eliminate this relationship and in that case it may have contributed to the results shown in Table 5.

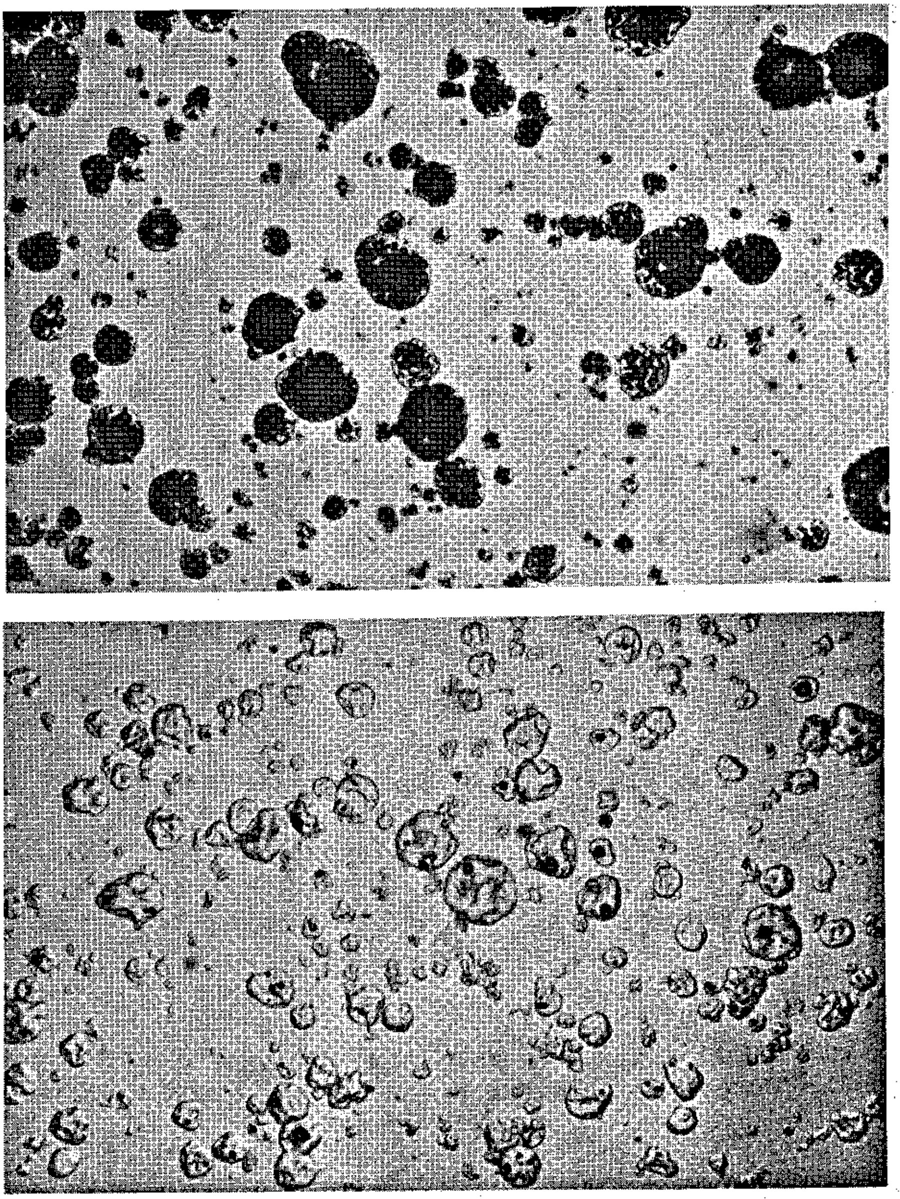

Fig. 5. Microphotographs of disc-sprayed skim milk powder particles. A (top): normal atomization; B (bottom): air-free atomization. Magnification × 100.

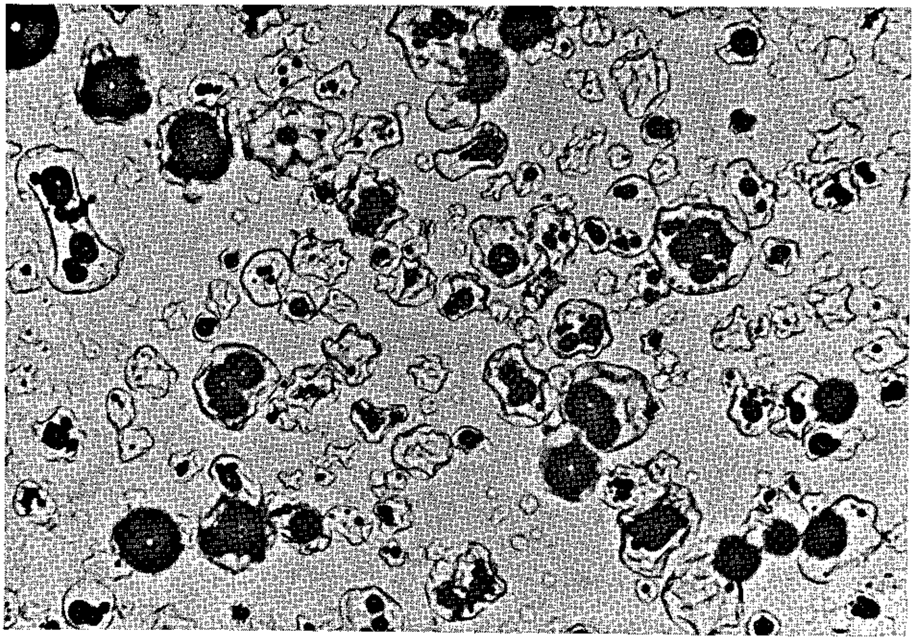

Fig. 6. Normal pressure-sprayed skim milk powder. Magnification × 100.

3.3.4 Properties of the powders. Some experiments were carried out on the efficiency of gas packing of whole milk powder, prepared either by normal or by air-free atomization. A single gas treatment of the latter powder compared favourably with the usual double gassing of ordinary powder.

Preliminary observations on the wettability of comparable sieve fractions of normal and air-free skim milk powders indicated that the absence of vacuoles significantly improves this property.

Finally a few comments will be made about the microscopical appearance of vacuole-free powders. When powder samples are observed microscopically as described earlier (1), the vacuoles appear as black spots in the transparent particles. Thus, the effect of air-free atomization upon the vacuole volume can be seen quite clearly in Fig. 5. Particles of normal disc-sprayed skim milk powder contain more vacuoles than normal pressure-sprayed powder (Fig. 6). Of course this difference vanishes when air-free atomization is applied.

For observation with a scanning electron microscope, we used the technique described by Buma and Henstra (11). A relatively dense normal skim milk powder particle (disc atomization) is shown in Fig. 7 together with an apparently vacuole-free particle obtained by air-free disc atomization of the same concentrate.

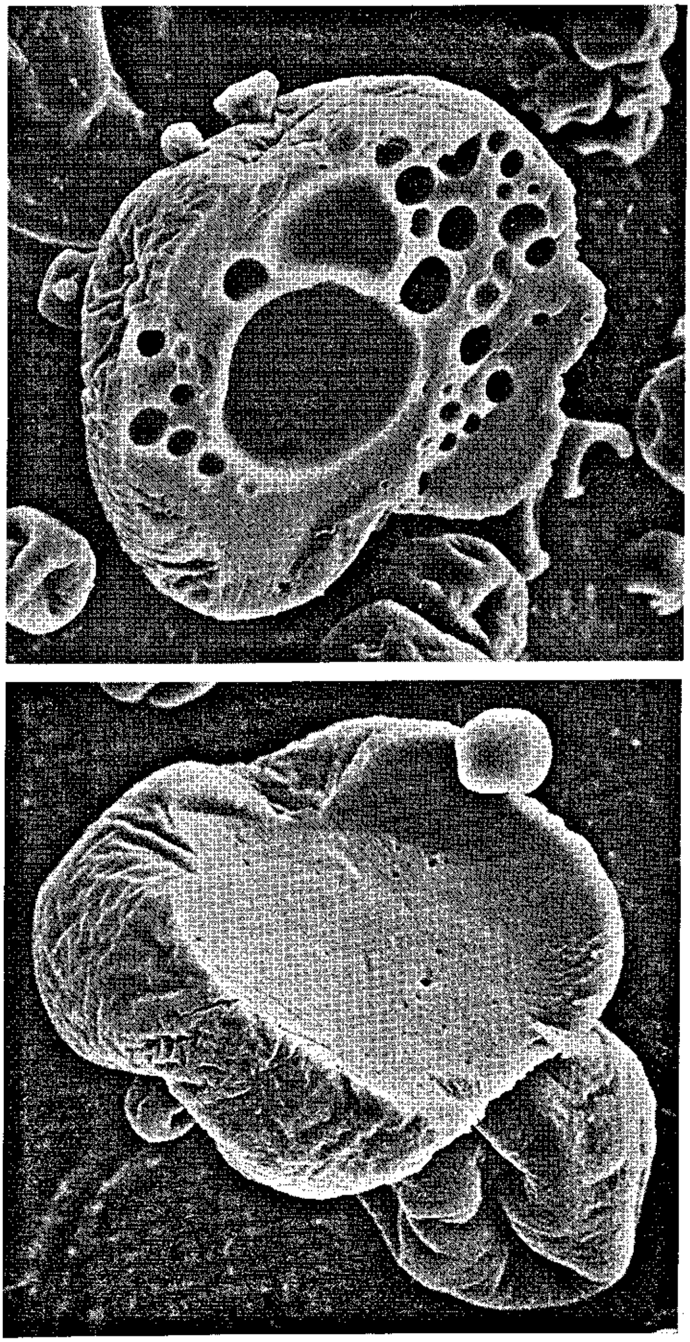

Fig. 7. Skim milk powder particles: Top: Normal disc atomization (magnification × 850); Bottom: Air-free disc atomization (magnification × 2600).

It will be noted that normal disc-sprayed powder particles (Fig. 5A) are fairly globular, but when the vacuole volume is small (Fig. 5B and 6), an irregular, dented surface is observed. Obviously, the primary explanation is shrinkage of the drying droplets. This is illustrated by Fig. 8, showing particles obtained by air-free disc atomization of unconcentrated skim milk. The same drying procedure applied to concentrated whole milk (41% total solids) yielded the powder shown in Fig. 9, where no severe denting is observed.

Such uneven shrinkage is a common feature of air-free powders consisting of milk solids, casein, maltodextrin, egg solids and others (Fig. 10). We tend to ascribe this primarily to the relatively low mass transfer rates within such

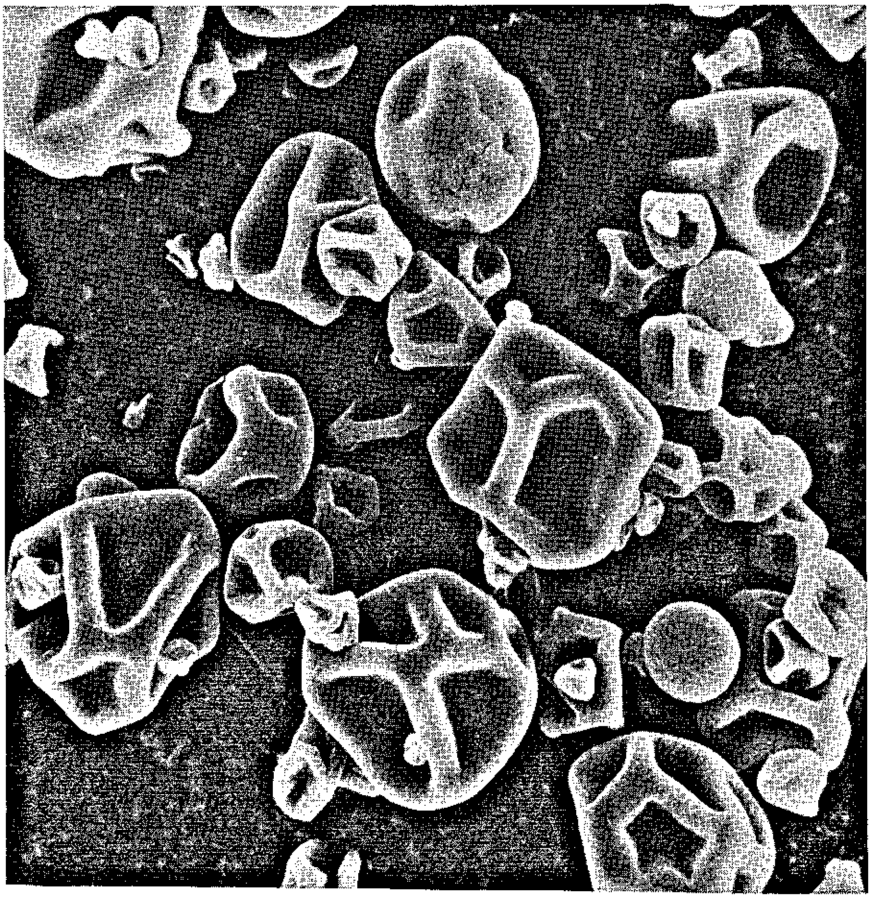

Fig. 8. Powder obtained by air-free disc atomization of unconcentrated skim milk. Magnification × 1150.

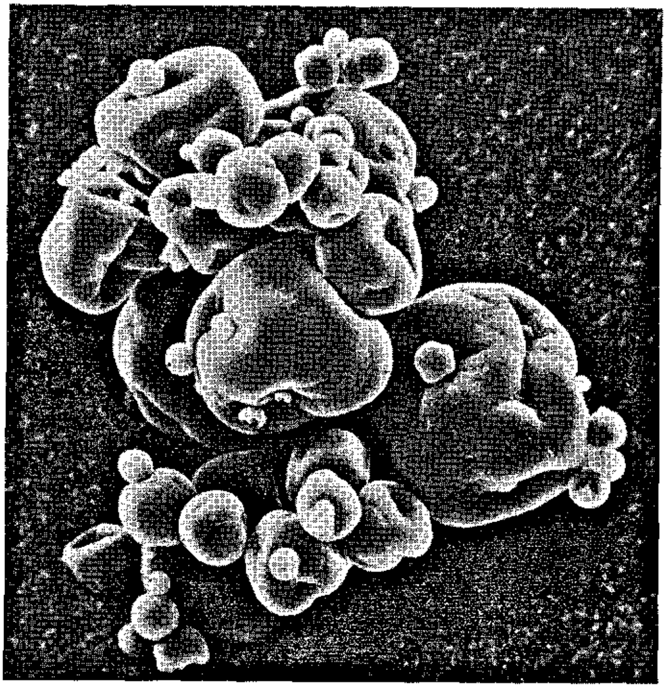

Fig. 9. Whole milk powder. Air-free atomization. Magnification × 700.

drying droplets, and this may well be related to the abundant presence of casein or other polymer molecules (12). Differences in the drying histories of individual droplets cause large differences between particles in one sample. Other interesting photographs are shown by Buma and Henstra (11, 12).

4 Conclusion

The conclusions formulated below pertain not only to the present paper, but also to the previous part of these studies (1).

Air incorporation. Before the actual atomization in a spray drier, air is dispersed into the liquid while it is flowing through (and leaving) the atomizer. The air present in the fresh powder does not originate from the collision of the drying air with the spray of droplets.

Vacuole initiation. Vacuoles are formed only in particles containing one or more gas bubbles that do not dissolve before the particle solidifies. This conclusion implies that vacuoles do not result from the spontaneous formation of vapour bubbles in the drying droplets.

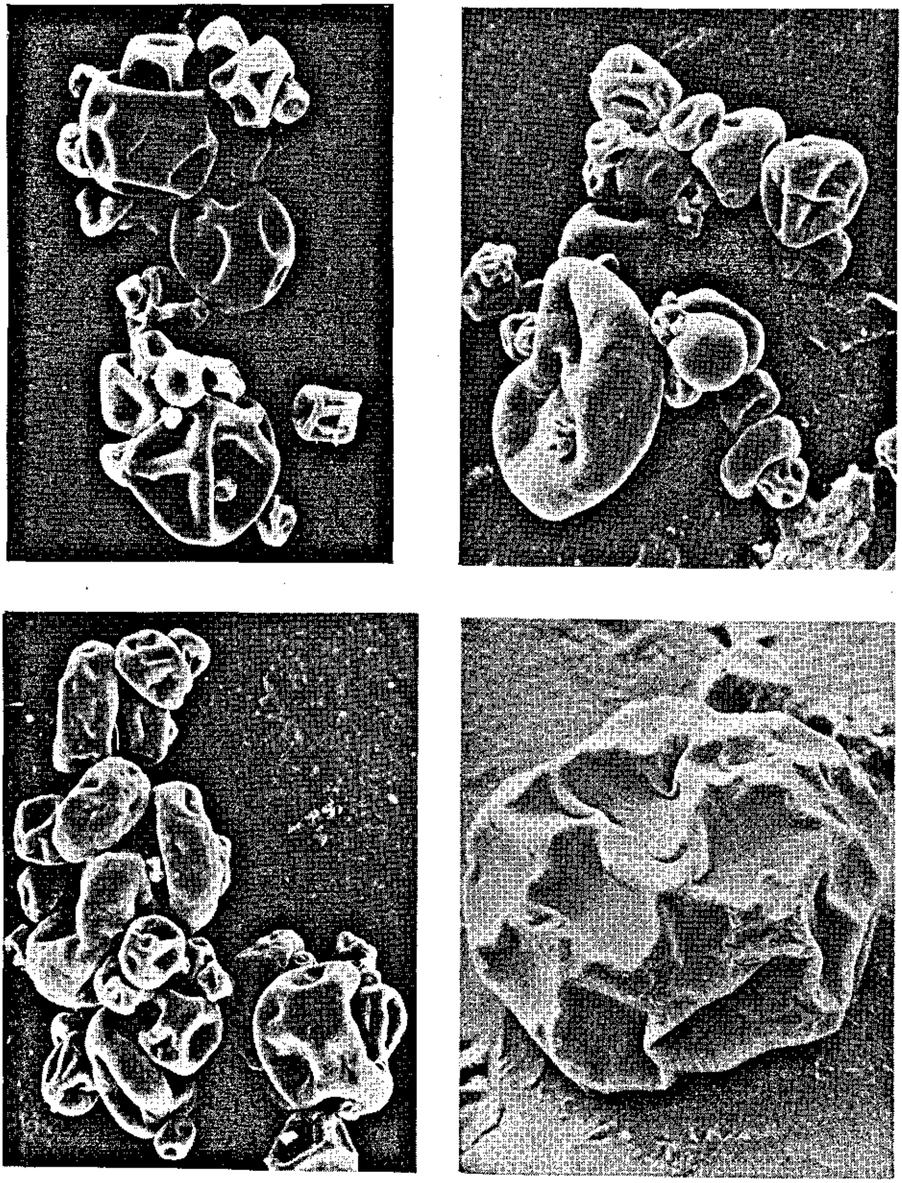

Fig. 10. Powder particles obtained by air-free atomization: A (top left) casein (magnification × 600); B (top right) malto-dextrin (× 300); C (bottom left) whole egg solids (× 370); D (bottom right) coffee (× 1500).

Bubble expansion. On average, the air bubbles present in the original droplets expand during drying of the droplets and this process results from case hardening, which is the combined effect of: 1) fast heat and mass transfer at the droplet's surface (evaporation); 2) relatively slow mass transfer in the droplet (diffusion); 3) shrinkage of the droplet's liquid phase.

Vacuole volume. The vacuole volume is governed by: 1) the degree of foaming in the atomizer (related to type and design of atomizer, properties of the liquid, feed rate); 2) bubble expansion, related to drying conditions such as drier design, air temperature and properties of the feed liquid.

Eliminating vacuoles. As long as the existing atomizers tend to cause foam formation, vacuole-free powders can only be made by replacing the air in the atomizer by a condensable vapour (steam).

Samenvatting

J. G. P. Verhey, *Vakuolenvorming in verstuivingspoederdeeltjes. 2. Plaatsbepaling en voorkoming van luchtinslag*

In het vorige verslag van deze studies (1) werd verondersteld dat vakuolen ontstaan door luchtinslag in de te drogen vloeistof gevolgd door uitzetting van deze luchtbellen. Dit tweede verslag behandelt hoofdzakelijk het eerste deel van dit proces, namelijk luchtinslag.

Twee reeksen proeven werden genomen. In de eerste reeks ging het erom de lucht in de vernevelaar te vervangen door koolzuurgas. In de zo bereide poeders vonden we dan voornamelijk koolzuurgas in plaats van de gebruikelijke lucht. Geconcludeerd werd dat in de diverse typen vernevelaars een zekere mate van luchtinslag ('schuiming') optreedt.

In een andere reeks proeven werd geen koolzuurgas maar stoom in de vernevelaar geblazen. Door de snelle condensatie van stoombelletjes in de drogende druppels werd de vorming van vakuolen kennelijk verhinderd. Hieruit volgde dat de aanwezigheid van gasbelletjes in de drogende deeltjes een noodzakelijke voorwaarde is voor de vorming van vakuolen.

Tenslotte worden in dit artikel enkele praktische aspecten behandeld van de bereiding van vakuolenvrije poeders door 'luchtvrije' verneveling.

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Vacuole formation in spray powder particles. 3. Atomization and droplet drying

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Summary

The model of vacuole formation, postulated in the previous reports, is compared with some considerations derived from basic theories. Air incorporation in the liquid during spraying is formulated as Kelvin-Helmholtz instability of the air-liquid interface in the atomizers.

Experimental evidence on the heat inactivation of enzymes during spray drying and other data are used for analysing the 'drying history' of individual droplets. Most of the drying appears to occur at rather low droplet temperatures. The possibilities for spontaneous formation of vapour bubbles (boiling) are found to be very small.

It is concluded that theoretical considerations lend support to the previous experimental results.

1 Introduction

In the previous reports of these studies we postulated a model of vacuole formation during the atomization and drying of spray droplets (1, 2). The model was based upon experimental evidence obtained by using a small drier. It was concluded that vacuoles originate from air bubbles incorporated during spraying which subsequently expand during drying as summarized in this paper (Section 3).

In this paper we shall again consider the process of vacuole formation, but it will now be done primarily on the basis of considerations derived from basic theories. From this point of view we will test the two possible mechanisms: 1) air incorporation followed by expansion of air bubbles, and 2) boiling under normal or reduced pressure.

With regard to the first mechanism we have to study the possibilities of air (bubbles) entering and leaving the liquid during spraying (Sections 4 and 5).

For estimating the chances that boiling might lead to vacuole formation, we

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need to know the temperature, pressure and concentration (elevation of the boiling point) inside a drying droplet as well as the possibilities for the nucleation of vapour bubbles. Therefore the entire 'drying history' of droplets should be analysed. In the last sections this will be attempted by combining certain data derived from basic theories with data from the literature on spray drying and with new experimental evidence.

2 Methods

In Section 8 some experiments are reported in which we used the following methods.

2.1 Rapid phosphatase test

As a routine check for proper pasteurization the phosphatase detection method of Aschaffenburg (3) is widely used in dairy practice, and on many occasions we also used this method. A negative test (proper pasteurization) implies that the activity of alkaline phosphatase in 1 ml of milk is insufficient to liberate more than 6 μg phenol from the substrate added. This means a reduction in the activity of the enzyme by at least 99% compared with raw milk.

2.2 Quantitative phosphatase determination

In some cases quantitative data on the phosphatase activity were needed and we then employed the method of Sanders & Sager (4). The result of this measurement is expressed as μg phenol liberated from a substrate by 1 ml of milk. Concentrated and dried products were diluted to the concentration of skim milk before the measurement.

2.3 Activity of rennin

Rennin activity was determined from the clotting time of a substrate (skim milk) to which the sample was added. We used Berridge's modified method (5).

All substrate solutions were prepared from one batch of spray-dried skim milk.

For the experiments on rennin inactivation we used whey rather than milk or skim milk as a carrier since, in the latter case, the activity measurement was hampered by clotting of the sample itself.

2.4 Heat stability of the enzymes at different moisture levels

The data on the thermal inactivation of enzymes usually apply to the normal, unconcentrated products such as milk. The study of such inactivation during drying obviously requires similar data for higher concentration levels. In the case of phosphatase inactivation in skim milk we secured such data from concentrated raw (unheated) skim milk as well as from moistened powders prepared from raw skim milk (see Fig. 2).

Samples of raw skim milk which had been concentrated to 63 % moisture at temperatures below 50 °C were subjected to various heating periods at 63 °C. The results (residual phosphatase activities) were equal to those obtained from unconcentrated raw skim milk.

The other points of the curve for phosphatase in Fig. 2 were determined by using samples of raw skim milk powder prepared from raw skim milk under mild conditions of spray drying so that no significant inactivation occurred. Samples of this powder were equilibrated in moist air to reach various moisture levels.

Small powder samples (1 g) were then sealed in plastic envelopes and heated for 5 minutes in water baths at various temperatures (intervals of 2 °C). Temperature equilibration in the samples was promoted by minimizing the volume of air in the envelopes. After the heat treatment the samples were dissolved in water and then the rapid phosphatase test (2.1) yielded the data shown in Fig. 2.

Inactivation of rennin in unconcentrated whey was determined after heat treatments in water baths and in a plate heat exchanger. The initial rennin concentration was taken higher than in nornal cheese whey, namely 10 ml rennet (strength 1 : 10 800) per kg whey.

The criterion of 50 % inactivation (Fig. 1) was chosen because the test method (2.3) is most accurate in this range.

The data on concentrated whey (Fig. 2) were secured after heating of the samples in water baths for different periods.

3 Description of the model of vacuole formation

During spraying the feed liquid is accelerated inside the atomizers to high velocities. Before the liquid leaves the atomizer, air bubbles of various size are dispersed into the liquid. This air-liquid dispersion or foam breaks up into droplets, probably via intermediate stages such as sheets and threads. This break-up will eliminate many air bubbles, especially the larger ones, but others will remain enclosed in the droplets formed.

Very severe drying conditions exist in the first stages of drying. They consist of large differences in velocity, vapour pressure and temperature between drying air and droplet. Evaporation is fast compared to the diffusion of water and solids inside the droplets, which causes large concentration gradients near the surface. This promotes the development of a high-viscosity surface layer and, eventually, of a rigid crust ('case hardening'). Evaporation continues at a sufficiently high rate to maintain the droplet temperature at a relatively low

Shrinkage of the droplet's surface compensates for the volume reduction level until most of the water has evaporated.
associated with evaporation. However this shrinkage is becoming increasingly difficult due to the continuing process of case hardening. Thus a stage is reached where a further volume reduction of the liquid is more easily achieved by expansion of air bubbles in the droplet's interior (if present) than by shrinkage of the solidifying surface .Hence, the resulting dried particles will contain vacuoles in which the air pressure is below atmospheric, even though the particle temperature has risen almost towards the temperature of the exhaust air.

In drying particles that do not contain air bubbles shrinkage occurs only at the particle surface and vacuoles will not develop. This condition promotes wrinkling and denting of the particle surface.

4 Air incorporation

If air incorporation into the liquid takes place in the atomizer, it is of interest to know the cause of the instability of the air-liquid interface in the atomizers. From the different types of hydrodynamic instability of interfaces as listed, for instance, by Gopal (6), the one that applies primarily to our case is the Kelvin-Helmholtz instability, 'which arises when two different liquids move with different tangential velocities across an interface' (6). This condition is certainly fulfilled in most atomizers, as will be discussed below. Kelvin-Helmholtz instability is stated to be dependent upon surface tension and viscosity.

4.1 Disc atomization

For a disc atomizer, the velocities of air and liquid moving through the disc can not easily be calculated and they will be very much dependent upon disc design. Peripheral (tangential) speeds are close to 150 m/s and for the radial velocity at the periphery of a small vaned disc values in the order of 10 m/s have been suggested (7).

The residence time of the liquid inside the disc is of the order of a second and as an example, the passage through the orifices of our disc lasts some 10^{-2} s. Hence, velocity differences last sufficiently long to corrugate the interface and produce a foam.

4.2 Pressure atomization

More distinct localization of air-liquid interfaces is possible in pressure atomization, viz. inside and outside the very top of the spray cone. The inside interface advances in the form of an air core through the nozzle orifice. The qualitative representation of the flow pattern in a nozzle orifice as given by Marshall (7) indicates that the liquid velocity at this surface is very high, possibly exceeding the velocities reached in disc atomizers. However, the residence time of the liquid at this very small interface is of the order of 10^{-5} s. The Kelvin-Helmholtz mechanism might cause air incorporation near the liquid surface. The flow in the orifice and the very short time available leave little chance for an even distribution of air bubbles through the liquid. If, furthermore, we consider the sizes of air bubbles and of droplets (roughly 1 % and 10 % of the orifice diameter), it appears quite possible that only the droplets originating at the inside of the spray cone would contain air bubbles.

The air-liquid interface at the outside of the spray cone begins at the steel surface of the nozzle. We may assume that the outer edge of the orifice acts as an active source of instability at this interface. Again this would concern only part of the liquid or the droplets. We found earlier (2) that a steam treatment of the spray cone from the outside is quite effective in preventing vacuole formation. Therefore we assume that air incorporation in pressure atomization occurs primarily at the outside of the top of the spray cone.

An important difference with disc atomization is that in pressure nozzles the conditions (particularly residence time) hardly allow for further disruption of newly formed air bubbles.

5 Loss of air

5.1 Disc atomization

The liquid flowing through an atomizer disc encounters increasing centrifugal force and a tangential acceleration. Both conditions will cause any air bubbles to move relative to the surrounding liquid. The terminal velocity of such bubbles in the centrifugal field (if reached) may be computed with Stokes' law. In this way a relative velocity of some 5 cm/s is found for a large bubble with radius 10^{-3} cm (liquid viscosity 1 Poise) located at the edge of our disc. For smaller bubbles lower velocities are found, proportional to the square of the radius. The bubbles were assumed to be at atmospheric pressure, but the pressure existing in the liquid will reduce bubble size and thus the actual velocities will be lower.

From these considerations it appears that only the bubbles larger than a certain critical size have a good chance of returning to the interface, where they will probably collapse and disappear rather quickly under the existing conditions. As an example, the large bubble mentioned above might escape from the liquid while it passes through the orifice in e.g. 10^{-2} s, by moving (relatively) 0.5 mm in that time.

Obviously, such a critical bubble size depends upon disc design and upon operational variables such as feed rate and properties of the feed liquid.

After leaving the atomizer the air-liquid dispersion is disrupted into droplets, and most of the air bubbles will disappear in the process. During the stage of disruption the conditions may seem to be quite favourable for Kelvin-Helmholtz instability (Section 4), but two inhibiting mechanisms are present. In the first place atomization causes a rapid expansion of the interface and this will tend to damp out corrugations of the interface. In the second place evaporation occurs during the actual atomization and this increases the viscosity and hence the stability of the liquid surface.

These views find support in a patent (8) describing the preparation of high-density disc spray powders by optimizing the conditions for loss of air. Immediately after leaving the disc, the spray is bent by a fast stream of air. Inertial forces will thereby remove the larger bubbles from the droplets. It is stated that the air stream should preferably be cool or humid in order to retard drying.

We have no knowledge of the practical applications of this patent and in fact we consider the suggested procedure of very limited value.

5.2 Pressure atomization

In pressure nozzles the probability of an air bubble returning towards the interfaces is small, due to (among other things) the short time available. This we concluded from calculations similar to those of the previous section. For the actual atomization the remarks given above are equally relevant.

5.3 Discussion

Air bubbles occupy some 5% of the volume of freshly atomized disc spray droplets of concentrated skim milk, and about 1% of the volume of pressure spray droplets (1). The number of bubbles in one particle can be estimated from microscopical observation to be of the order of 10 to 100 for disc atomization and around 1 for pressure atomization. For a droplet radius of 25 μm we then find average bubble radii of 4 to 2 μm (disc) and 6 μm (nozzle).

These facts can now be tentatively explained by differences in the occurrence of instable interfaces. Presumably the main differences are the time available for air incorporation and for bubble disruption as well as the degree to which the flow patterns promote mixing and bubble disruption.

6 Evaporation during deceleration

The initial velocities of the droplets leaving a disc atomizer are close to 150 m/s and similar velocities are reached in pressure atomizers (Section 4). The deceleration of such droplets by air friction has been studied by Sjenitzer (9). We applied his data to the conditions of our experiments and we calculated the time and the distance over which droplets are decelerated from 150 to 5 m/s. For droplets with diameters of 100, 50 and 10 μm we found times of 0.027, 0.009 and 0.0007 s and trajectories of 72, 28 and 2 cm, respectively. Evaporation is disregarded in these calculations and the droplets are considered as rigid spheres.

Hayashi (10) measured air temperature distributions in a spray drier and found that at least 75% of the total temperature drop (inlet temperature minus outlet temperature) occurred in a rather small area just around the disc atomizer. The same was observed by us and by several drier manufacturers (personal communications). The area where the air temperature falls sharply coincides with the area where the spray decelerates.

This rather simple information is of great importance. The sharp temperature decline in the deceleration area results from two mechanisms: evaporation and mixing. If evaporation were solely responsible, we should conclude that most of the water evaporates from the droplets in this area, in a period of little more than roughly 10^{-2} s. It would then also follow that the droplet temperature is low during deceleration because of the high evaporation rate.

If thorough mixing of the air in the drying chamber were to account for the falling temperature, the droplets would be drying in relatively cold air (close to the exhaust temperature) and so they would again be relatively cool while evaporating in this air. This supposition implies that the rate of mixing in the drier is high compared with the overall flow rate of drying air. As a consequence, the air velocity in the drying chamber should be much higher than the velocity of the incoming hot air (which lies, usually, between 5 and 10 m/s). This seems rather improbable. Moreover the mixing action of a rotating smooth disc is small and the atomized liquid causes mixing only during deceleration. It is to be expected that in large commercial equipment mixing is of even less significance than in a small drier like ours.

Our conclusion is that the sharp temperature decline in the deceleration area results mainly from evaporation and that at least some 50% of the total evaporation takes place in this relatively small area in roughly 10^{-2} s.

Obviously the high evaporation rate during deceleration results partly from the high velocity of the droplets relative to the incoming hot air.

7 Drying temperature

7.1 Preliminary observations

7.1.1 Direct temperature measurements in the drying drops. Several investigators recorded the weight and the temperature of single drops that were drying under well defined conditions (e.g. 11, 12). Such data could then be compared to those calculated theoretically. Good agreement may be found but we tend to consider such data of little relevance to the actual spray drying process. The main objection is that the drying rates in these experiments are necessarily lower by a factor of about 10^4 than in the essential first phase of spray drying. Therefore the transport equations checked and approved by these experiments need not be valid for spray drying.

7.1.2 Earlier theoretical computations. A theoretical approach to the spray drying process basically consists of solving a set of heat and mass transfer equations. The value of such work greatly depends upon the assumptions (simplifications) on which the model is based, and upon the values used for the different parameters involved.

Rather high droplet temperatures (viz around 100 °C or even higher) are often computed, theoretically, in the following way. A high rate of heat transfer toward the initially homogenous droplet causes vigorous evaporation. Since diffusion within the droplet is relatively slow, the water content at the droplet surface becomes very much lower than in the interior. Consequently the vapour pressure of the surface layer drops sharply. This lowers the evaporation rate and the cooling effect of evaporation. The continuing fast heat transfer from the surrounding air then heats the droplet to a high temperature.

Undoubtedly, this reasoning is qualitatively correct. Nevertheless several errors can be imagined and we shall pay attention to two of them.

Firstly, the computations often predict the existence of an extremely thin, 'dry' surface layer in an early phase of drying (13, 14). Apart from the possible occurrence of cracks due to shrinkage during the formation of this film, it appears rather unrealistic to believe that such a film would be able to shrink while remaining globular and homogeneous. Instead, it would either break or dent and so the assumed spherical symmetry of the droplets would no longer exist.

Secondly, in the computations the droplet is considered a continuum, but this assumption might become unacceptable when extremely steep concentration gradients occur (as in the case just mentioned). In such cases concepts of statistical mechanics rather that those of continuum theory should be used.

7.1.3 Previous experiments on spray drying. We had observed previously that the heat damage during spray drying of milk was less than during pasteurization for 15 s at 72 °C (see also Table 5 of Part 2 of these studies (2)). The criterion for proper pasteurization is a negative phosphatase test (Section 2.1). Such a negative test could not be obtained by normal spray drying of concentrated raw milk, unless high drying temperatures and very low feed rates were used. In particular the outlet temperature of the drying air had to be well over 100 °C.

The temperature history of the droplets can not be derived from these experiments unless other variables such as time and water content are taken into consideration, and we therefore continued the experiments.

7.2 Heat inactivation of enzymes during spray drying

7.2.1 General

A correct interpretation of data such as those given in Section 7.1.3. is not possible without knowledge of the effect of water concentration upon the heat sensitivity of the enzymes. Therefore we determined this relationship (Section 2.4) and the result appears in Fig. 2. This information is also presented in Fig. 1, together with the well known log time-temperature plot for phosphatase inactivation (15). Included in these figures are data on the inactivation of rennin, which were obtained because this enzyme is more sensitive to heat than is phosphatase (Sections 2.3 and 2.4). This is true only for high water contents, as Fig. 2 shows.

The data of Fig. 2 suggest that high solids concentrations protect the enzymes against heat, especially in the case of rennin. The concentration of the enzymes themselves (which increases with the solids concentration) probably plays no role because the activity measurements took place after dilution of the samples.

7.2.2 Phosphatase inactivation

In one series of experiments we studied the inactivation of native alkaline phosphatase by the spray drying of concentrated raw skim milk. We chose a feed liquid containing 30% total solids because at this level the enzyme has the same heat sensitivity as in skim milk (Fig. 2).

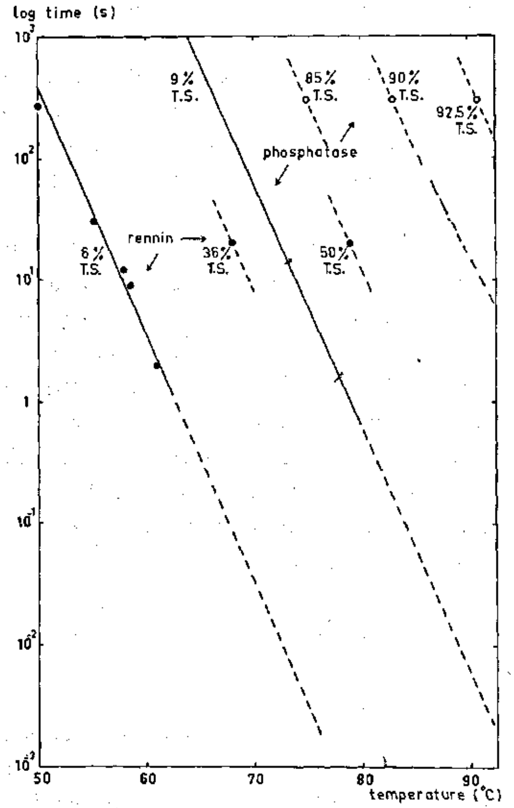

Fig. 1. Minimum time-temperature combinations for obtaining a negative phosphatase test or 50% reduction of rennin activity. The data for phosphatase pertain to raw skim milk (9% solids) and to humidified raw skim milk powders; the data for rennin pertain to whey and concentrated whey.

The results are summarized in Fig. 3. When the feed rate is kept constant (line 1) the outlet air temperature rises together with the inlet temperature and considerably increasing inactivation is found. We isolated the effect of the inlet temperature by adjusting the feed rate to maintain certain outlet air temperatures

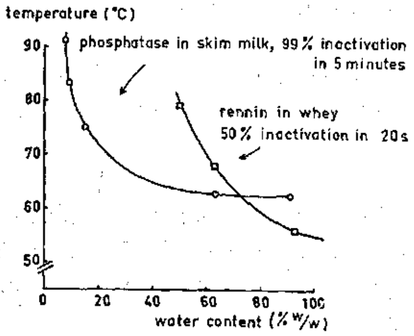

Fig. 2. Minimum heating temperatures (during times as specified) for obtaining certain reductions of enzyme activity.

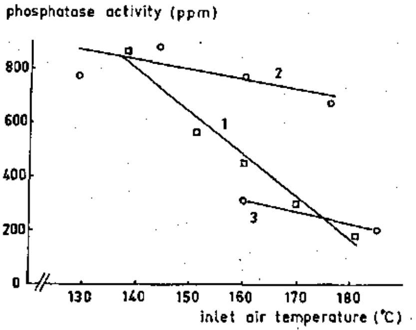

Fig. 3. Phosphatase activities of powders produced from concentrated raw skim milk (phosphatase activity 1300 μg/ml) at different inlet air temperatures. 1: outlet air temperature varies from 103 °C (left) to 140 °C (right); 2: outlet air 100 °C; 3: outlet air 125 °C.

(lines 2 and 3). It appears from the figure that roughly 75% of the observed temperature effect must be attributed to the outlet air temperature.

The reduction in the phosphatase activity in all these powders varies from 30 to 85%. Since the data of Fig. 1 apply to 99% inactivation it is of value to note that the line for 50% inactivation should be located some 7 °C to the left of the line (9% T.S.) in Fig. 1.

7.2.3 Rennin inactivation. When concentrated whey to which rennin was added was spray-dried under any of the conditions reported in Fig. 3, we always found an unchanged rennin activity in the powder. This is not surprising since at low moisture levels this enzyme is less sensitive to heat than is phosphatase (Fig. 2). Therefore we also dried unconcentrated whey (6% solids). Again the enzyme completely survived except for one powder prepared at 183 °C inlet and 131 °C outlet air temperature, where 25% reduction was measured.

7.3 Discussion

When interpreting the results of this section, we encounter a number of problems. The deceleration phase (Section 6) last some 10^{-2} s and thus we are interested in this time level in Fig. 1. There we have only extrapolations because of rather obvious experimental limitations. We see no reason, however, why extrapolations down to 10^{-3} s should not be justified.

Other problems arise from the fact that in drying droplets the temperature and moisture distributions are uneven and rapidly changing. Nevertheless we can formulate certain suppositions and then we see how they fit into the data.

In the first place we might assume that the enzymes are inactivated while they are most vulnerable, that is while the moisture content is still high. It might be that during deceleration the droplet temperature rises while the moisture content in the interior is still almost unchanged. We would then expect (Fig. 1) that rennin in unconcontrated whey would be more inactivated than would phosphatase in skim milk. Furthermore a strong effect of the temperature of the inlet air would be most probable.

The observations in the previous sections are quite contrary to these expectations and it must be concluced that the detected heat effects do not primarily take place during deceleration. Consequently, Fig. 1 indicates that in this phase, under normal conditions (exhaust temperature 100 °C), the droplet temperature does not rise beyond 60 to 70 °C (Fig. 1).

The wet bulb temperature of the inlet drying air lies around 45 °C, as can be read from a psychrometric chart. Since the water activity of the feed liquid is some 10 to 15% lower than for pure water, the minimum drying temperature of the feed liquid will be around 50 °C, which is not far from the upper limit given above. Therefore it must be assumed that the water activity of the droplet surface does not decrease very much during decerelation. From Fig. 3 it follows also that the inlet air temperature hardly affects the droplet temperature in this phase.

As a second supposition we may consider the last phase of drying, because it lasts a relatively long time. If the moisture content in this phase were to average some 10%, phosphatase inactivation might be possible (Fig. 1). But from Fig. 2 it appears improbable that rennin should be inactivated in this phase.

If the outlet air temperature is well over 100 °C, phosphatase inactivation may be possible up to the very last drying phase (Fig. 1). At normal outlet temperatures (e.g. 90 °C) however, no phosphatase inactivation can be expected in the dry particle.

Therefore we tend to believe that normally most of the heat damage occurs in an intermediate phase when the moisture content in the interior of the droplet is, say, half of the initial value. In this phase the outlet air temperature

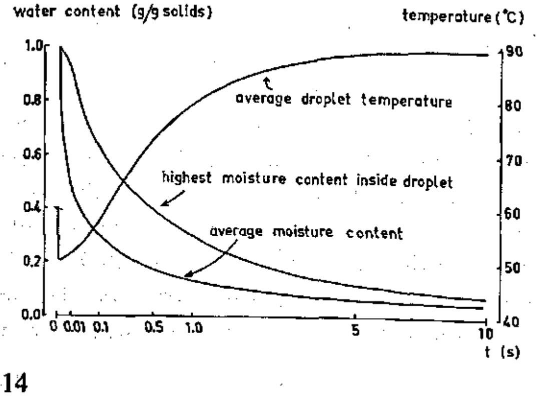

Fig. 4. Suggested average 'drying history' for droplets of average size under normal spray drying conditions. Feed liquid temperature 60 °C, outlet air temperature 90 °C.

may be decisive for the droplet temperature (Fig. 3) because the water activity at the droplet surface has then become rather low so that the cooling effect of evaporation is weak.

7.4 Drying history

It may seem premature to construct a drying history of single droplets, based upon the rather limited evidence produced so far. Nevertheless we present a graphical illustration of our opinion in Fig. 4. It may help the imagination and stimulate the discussion. Some of its features will be briefly mentioned.

Whatever the initial temperature of the feed liquid, it will very quickly assume the 'wet bulb temperature' of this liquid, that is estimated to be 50 °C in our case. The outlet temperature of the drying air (related to inlet air temperature, feed rate, water content, etc.) primarily governs the rest of the temperature curve. Of course the properties of the drying liquid (diffusion rates, surface characteristics during drying) also play an important role.

In the curve for the average moisture content the conclusion in Section 6 may be recognized. The highest moisture content in the droplets will be much dependent on the transport properties of the liquid. We believe that in the case of milk heat damage will occur mainly between 0.1 and 1 s after atomization. The partial air pressure in the air bubbles will mostly decrease in this same period, because case hardening is then becoming important.

8 Vapour bubble formation

Boiling of water in a drying droplet may occur if two conditions are both fulfilled. In the first place the local temperature must reach the local boiling temperature, which depends upon water concentration and pressure. In the second place, if no suitable nuclei such as air bubbles are present, boiling requires nucleation. For the spontaneous formation of a tiny vapour bubble an energy threshold has to be passed and therefore the actual boiling temperature must be exceeded. In a dispersed phase, such as a spray, many nuclei are required before boiling can play a significant role.

The number of vapour bubble nuclei which will be spontaneously formed per unit volume and time can be roughly calculated from the theory of homogeneous nucleation (16). Assuming an enthalpy of vaporization of 550 cal/ml water and a surface tension of 50 dyne/cm, we can roughly calculate nucleation rates. For instance, if the boiling point is exceeded by 10 °C, about 10^{-10} nuclei $cm^{-3}\ s^{-1}$ would be formed. This number is very much dependent upon temperature. When the temperature is 5 °C higher, the rate rises to $10^{14}\ cm^{-3}\ s^{-1}$.

Since we have some 10^7 droplets per ml, spontaneous nucleation will not play a role unless the local boiling temperature is exceeded by some 13 °C. For concentrated skim milk the elevation of the boiling point is several °K and it increases during drying.

Obviously the spontaneous formation of vacuoles by this mechanism requires rather high droplet temperatures or very low pressures within the droplet, or certain combinations of both. During the deceleration phase the conditions of time (Section 6), temperature (Sections 6 and 7) and pressure are certainly inhibitive for spontaneous nucleation. Later on the concentration (hence boiling temperature) rises, but more time is available and low pressures may occur; on the other hand nucleation may be much retarded because of the very high viscosity. If this mechanism were to cause vacuole formation, it should occur at this stage.

Experimentally we reached the conclusion that vacuoles do not develop in the absence of air bubbles (2). After the above considerations this is hardly surprising.

9 Discussion and conclusions

It may be concluded that theoretical considerations support our empirical model of vacuole formation summarized in Section 3. From Sections 6, 7 and 8 the spontaneous formation of vapour bubbles appears rather improbable. On the other hand the theory of unstable interfaces (Section 4) indicates that air incorporation is quite possible during spraying, that is to say, prior to the actual atomization.

The suggested temperature history of droplets (Fig. 4) shows that air bubbles might undergo thermal expansion of about 10% by volume. The forces acting on the surrounding liquid are expected to be of much more importance for bubble expansion. Probably it is correct to state that expansion results from case hardening in the last phase of drying, which was previously concluded from our experiments.

Apart from the conclusions on vacuole formation, other aspect of droplet drying must be mentioned.

We are confident that the suggested drying history (Fig. 4) is generally correct. The temperature curve is not only supported by evidence given in Sections 6, 7.2 and 7.3, but also by practical experience. As an example we mention the spray drying of egg solids, which can easily be done without damaging the very heat sensitive egg proteins. Our doubts with regard to the higher temperatures calculated theoretically were given in Section 7.1.2. On the other hand it must be admitted that our data do not provide absolute proof because they, too, contain certain weaknesses, for example the extrapolations in Fig. 1 and the small amount of data given in Fig. 2.

Acknowledgments

A significant contribution to the production of this paper was given by Dr P. Walstra. For his stimulating advice throughout these studies I am very grateful indeed.

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The numerous experiments in these studies were performed with great skill and enthusiasm by Mr H. J. van der Stege and Mr W. L. Lammers.

Of the many photographs, kindly taken by Mr. S. Henstra (Technical and Physical Engineering Research Service, Wageningen) with the scanning electron microscope, some have been published in Part 2 of these studies.

Samenvatting

J. G. P. Verhey, *Vakuolenvorming in verstuivingspoederdeeltjes. 3. Het vernevelen en de droging van druppels*

Het model van vakuolenvorming, opgesteld in de vorige artikelen van deze reeks,wordt getoetst aan theoretische beschouwingen, mede op grond van enige aanvullende experimenten. Luchtinslag in de vloeistof tijdens het vernevelen wordt omschreven als Kelvin-Helmholtz-instabiliteit die optreedt aan het lucht-vloeistof-grensvlak in de verstuivers.

Experimentele gegevens over de hitte-inaktivering van enzymen (fostatase en stremsel) bij verstuivingsdrogen worden samen met andere gegevens gebruikt voor een analyse van de 'drooggeschiedenis' van afzonderlijke druppeltjes. De droging blijkt grotendeels bij vrij lage temperaturen plaats te vinden. De mogelijkheden voor de spontane vorming van dampbellen (koken) blijken zeer gering te zijn.

De konklusie is dat de theoretische beschouwingen steun verlenen aan de op experimentele gegevens gebaseerde hypothese, namelijk dat vakuolenvorming een gevolg is van luchtinslag tijdens het vernevelen, voorafgaand aan de feitelijke druppelvorming.

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A method for measuring the particle density distribution of spray-dried powders

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Summary

This paper describes the preparation and utilization of liquid density gradient columns. Such columns appear to be a useful tool for studying the distribution of the apparent particle density of individual powder particles. Several applications of the method are described and illustrated with photographs. It is shown that this method gives a more detailed insight into the effect of certain conditions during spray drying and into general characteristics of certain powders.

The method is of course only suitable, basically, for those powders which are practically insoluble in the liquids used in the column.

1 Introduction

Microscopy of milk powders justifies the general statement that no two particles are identical. A study of the differences between individual particles with regard to certain properties might be very useful. The present paper only deals briefly with the apparent density of individual particles.

The average apparent density of a powder sample is used for computing average vacuole volumes. On several occasions during our studies on powder structure it was deemed useful to consider not only an average vacuole volume but also the distribution of this parameter over individual particles. This can be done using Verhoog's sedimentation method (1), in which powder samples are centrifuged in homogeneous liquids of varying density. This method can be modified to yield density fractions when the sediment obtained from a low density fluid is resuspended in a denser fluid and so on.

When a direct visual presentation of particle density distributions is wanted, a suitable method is available in the form of density gradient columns. The principle of preparing and using density gradient columns can be found in physical

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handbooks and they are receiving increased attention in advanced techniques of centrifugal fractionation (2).

2 Method

2.1 Description

We constructed an outfit for preparing gradient columns that is shown 'ready for use' in Fig. 1. When the stirrer is started, the stopcocks opened and the pump switched on, each tube will be gradually filled with a liquid of continually decreasing density in which each powder particle may rise toward its equilibrium position.

2.2 Notes

2.2.1. The low-density fluid consisted of 79% w/w toluene and 21% w/w carbon tetrachloride (density 0.96 g/cm^3) and the high density fluid was pure carbon tetrachloride (density 1.60 g/cm^3).

The choice of the two liquids was based primarily upon their hydrophobic nature so they would not dissolve any constituents of the powders except fat, and upon the required density range (see also Section 3.5). Other desirable features of these liquids are a low viscosity and a low surface tension. Before use, the liquids were dried for a week with magnesium sulphate.

2.2.2 After filling the tubes were centrifuged in a Gerber type centrifuge (2 min at 800 rev/min, swing-out rotor) to ensure that each particle reached its equili-

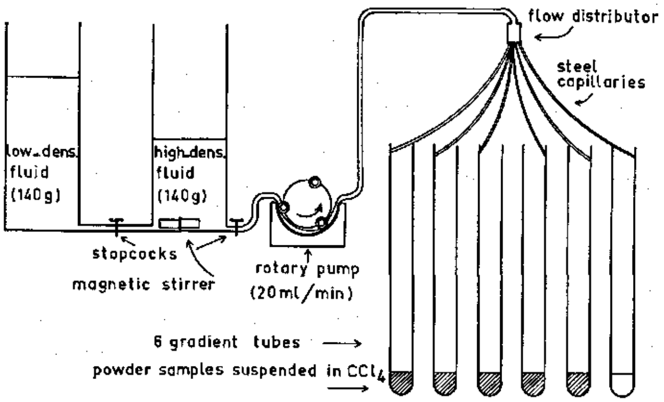

Fig. 1. The preparation of density gradient columns. Explanation in the text.

brium position and that any loose clumps of particles were broken up. For this reason we used tubes of the type shown in Fig. 1 (internal diameter 17 mm, nominal volume 45 ml).

2.2.3 The absence of air bubbles in the flow distributor is essential for achieving an even distribution. Therefore we first operated the pump at a higher speed, removing about 18 g of carbon tetrachloride from the mixing vessel (the left hand stopcock being closed). In this way the position depicted in Fig. 1 was reached and the left hand stopcock opened at that stage. Thus the actual procedure was slightly more complicated than Section 2.1 would suggest.

2.2.4 The powder samples (0.30 g) were weighed into the well cleaned and dried tubes before the gradient columns were prepared. This sequence was preferred to the opposite one, since in the latter case the gradient could be disturbed by the sinking of the powder mass, and also because some powder sometimes adhered to the wall.

2.2.5 Calibration was carried out by introducing small drops of aqueous ferric chloride solutions of known density into an 'empty' column. One such column is shown in Fig. 2A and the gradient appears non-linear. This is probably due to inadequate stirring in the mixing vessel.

2.2.6 When the prepared columns are kept standing for several hours, flocculation of powder particles becomes plainly visible. Therefore any further analysis should not be delayed.

2.2.7 The columns can be visually compared or photographed and for a more quantitative characterization optical techniques such as light scattering may be employed. The columns can also be fractioned by removing successive layers by means of suction. Stirring and centrifugation of such fractions will result in a further separation of the powder into two density fractions. It is also possible to add some toluene to a fraction followed by sedimentation of all the particles.

For microscopical analysis small samples may be drawn from certain levels with a pipette or a glass capillary and if necessary the sample can be concentrated by evaporation in a dessicator, dried on a slide glass and suspended in paraffin oil.

2.2.8 Due to inaccuracies in the flow distribution the height of individual columns varies somewhat. We introduced calibration drops into columns of different height and expressed drop level as a percentage of column height.

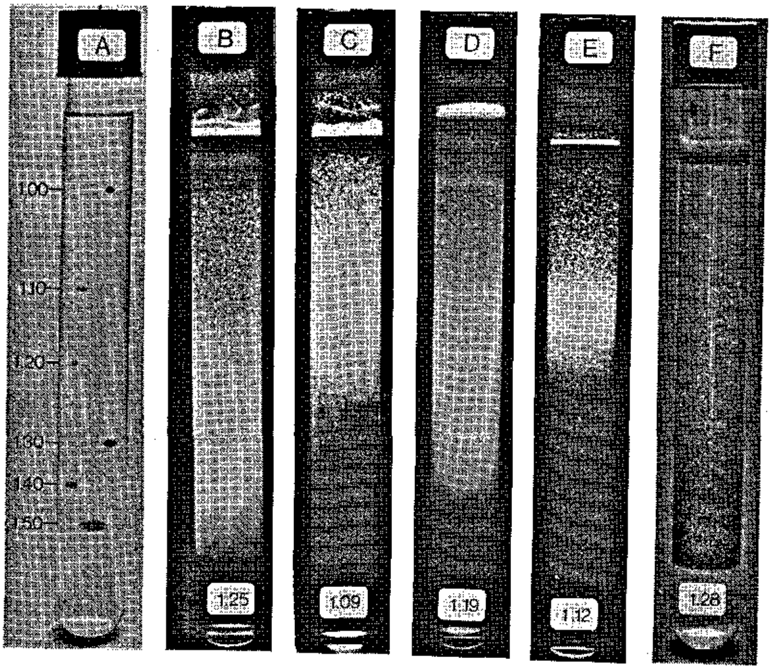

Fig. 2. Some examples of powders in density gradient columns. A. Calibration column; B. Commercial skim milk powder, factory X; C. Commercial whole milk powder, factory X; D. Commercial skim milk powder, factory Y; E. Instantized skim milk powder, factory Y; F. Spray-dried coffee extract.

These 'relative' drop levels appeared independent of column height. This should be remembered when comparing columns of different height.

3 Some applications

3.1 General

In the photographs (Fig. 2–6) the apparent particle density (ϱ_a) of each powder, as measured with the air comparison pycnometer (3), is indicated beneath each column.

Fig. 2 shows a calibration column (A) and some commercial powders. Any particles with densities lower than 0.96 g/cm^3 are floating on the surface or adhering to the glass wall. Usually only a few particles are observed in the area directly below the surface. This is partly due to the fact that in this area the density differences are small.

When the powder 'cloud' has a sharp bottom line (column B) then this line

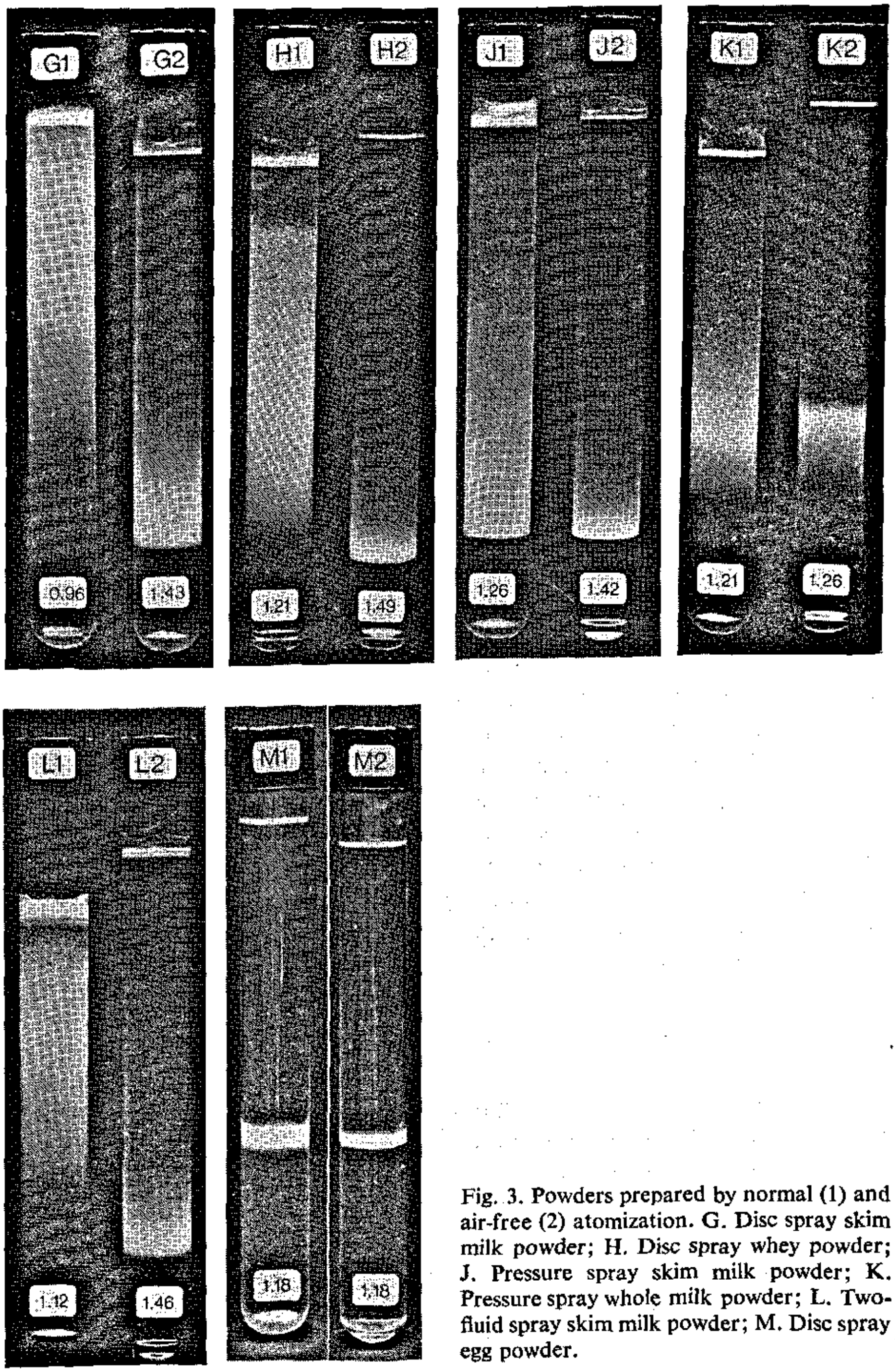

Fig. 3. Powders prepared by normal (1) and air-free (2) atomization. G. Disc spray skim milk powder; H. Disc spray whey powder; J. Pressure spray skim milk powder; K. Pressure spray whole milk powder; L. Two-fluid spray skim milk powder; M. Disc spray egg powder.

indicates the true density of the powder and the particles located here are free of vacuoles. This is true for skim milk powders, but in the case of whole milk the solution of the free fat will increase the density of the particles except for those whose density is lower than the density of the fat.

Column D and E of Fig. 2 show the effect of agglomeration upon the density distribution. The density of agglomerates varies less than the density of the original particles because each agglomerate consists of particles with different densities.

3.2 Air-free atomization

Fig. 3 shows that density gradient columns are remarkably suited for displaying the effect of air-free atomization. For each pair of powders the processing conditions were equal except for the steam treatment at the atomizer (4).

Many skim milk powder particles are observed on top of the liquid, and air-free atomization does not remove this fraction quantitatively. Column J2 shows a more or less continuous density distribution whereas in columns G2 and L2 particles of intermediate density seem to be missing on the photographs, but in the tubes we did observe a few of them.

When a fresh preparation of normal egg powder in paraffin oil is observed microscopically, most particles show a large vacuole (5) which disappears upon standing. Apparently the permeability of the particle wall allows the penetration of paraffin. It is evident, then, that our density liquid will penetrate more rapidly; in the air comparison pycnometer no vacuoles will be detected at all. This is in agreement with the appearance of the powder layers in the columns M of Fig. 3, their height indicating their packing density. Both layers are located at a level of $\varrho = 1.38$ g/cm^3 due to extraction of fat. Apparently the rather mild extraction during preparation of the columns suffices to remove all the fat, regardless of the vacuole volume.

3.3 The effect of the inlet temperature of the drying air

The apparent density ϱ_a of a spray powder rises when the inlet temperature of the drying air is lowered (6) .For the powders represented by the series N and P in Fig. 4 these air temperatures were 170, 155, 140 and 125 °C, respectively.

In the case of disc atomization the whole density distribution varies with the air temperature. The material in the lower part of the column (high density) consists largely of broken particles and particle fragments (see Section 3.4).

The pressure spray powders (P) show a stronger increase of ϱ_a when the air temperature decreases, but in all four columns a more or less constant high

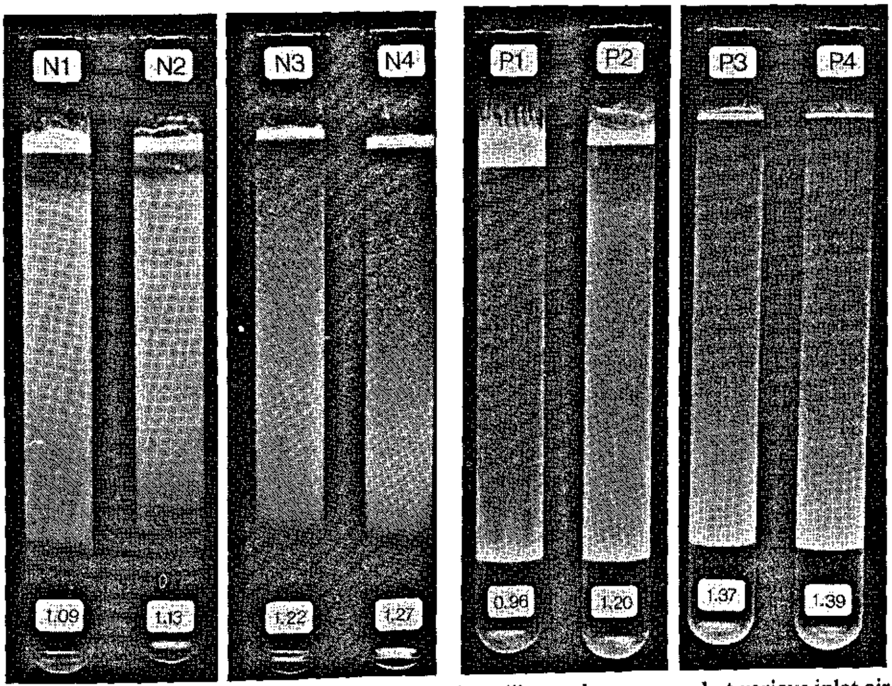

Fig. 4. Disc spray (N) and pressure spray (P) skim milk powders prepared at various inlet air temperatures,
1. 170 °C; 2. 155 °C; 3. 140°C; 4. 125 °C.

density fraction is present. The latter is a characteristic difference between the two systems of atomization.

3.4 Grinding of powders

If a particle containing many vacuoles is broken into a few pieces then each piece will probably have a higher density than the original particle but it may still contain many undamaged vacuoles. This is what happens, roughly, if a disc spray skim milk powder is ground under moderate conditions. We used a Kenwood 'Kenmix 55' mixer, not very different from an electric household coffee-grinder, and took the photographs shown in Fig. 5, columns Q. The whole powder cloud slowly moves towards higher densities after prolonged grinding. Air-free particle fragments were only faintly visible in column Q3.

A rather different picture results from grinding a similar pressure spray powder (Fig. 5, columns R). The powder cloud roughly maintains its position even though ϱ_a increases much more than in the disc spray powder. However, the

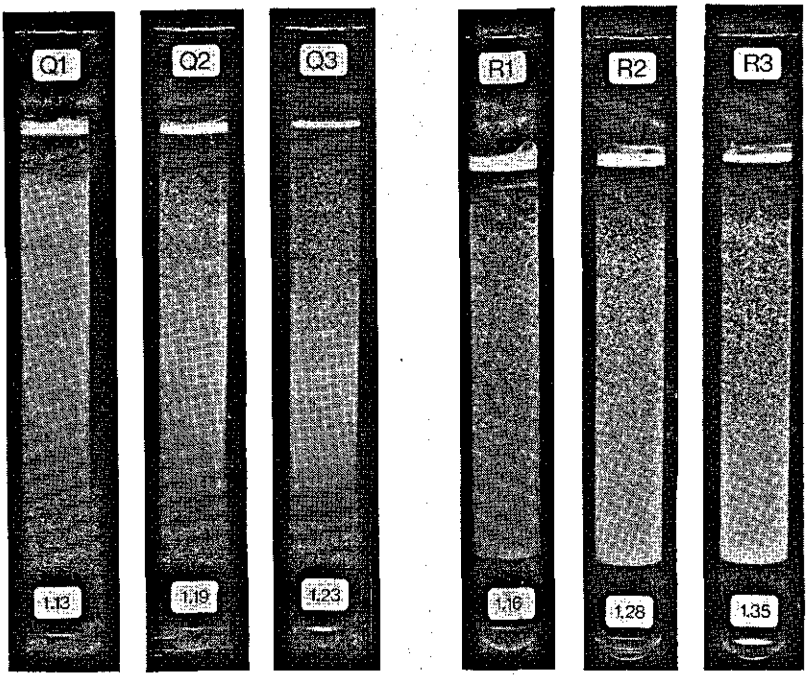

Fig. 5. Disc spray (Q) and pressure spray (R) skim milk powders. 1. Normal; 2. After 1 min grinding; 3. After 5 min grinding.

layer of low-density particles floating on column R1 almost disappears upon grinding and the fragments move towards the region of highest density. The explanation is easy: pressure spray particles contain few vacuoles and the low-density particles, often 'balloon-shaped', break into virtually air-free fragments.

Incidentally, it is noted that we could achieve complete mechanical disintegration of particles only if a ball mill was used.

3.5 Density gradients of different range

The density range of our gradients may be extended by using a lighter fluid instead of toluene. In this way most of the particles now floating on the surface may be incorporated in the column. On the other hand we may wish to reduce the total density interval if we are interested in the very densest particles.

As an example Fig. 6 shows some columns in which the density ranges from about 1.40 to 1.52 g/cm^3. The calibration columns show an almost linear gradient now that the density differences in the mixing vessel (Fig. 1) are so much smaller.

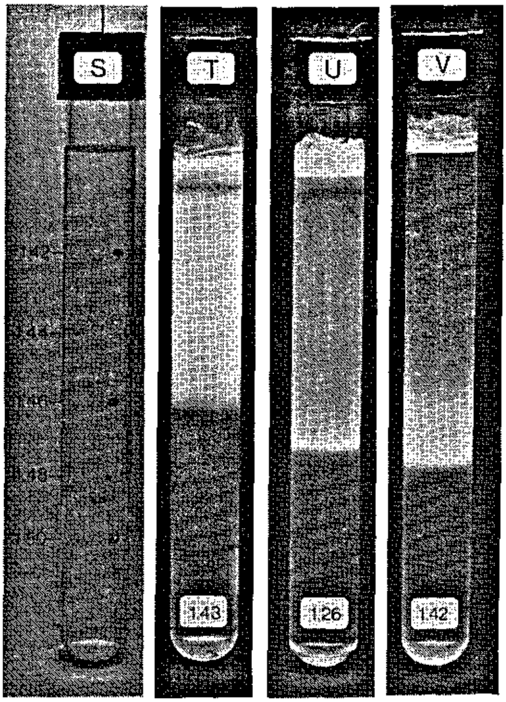

Fig. 6. Density gradient columns of small range. S. Calibration column; T. Disc spray skim milk powder, air-free atomization (= powder G2); U. Pressure spray skim milk powder (= powder J1); V. Same as U, but with air-free atomization (= powder J2).

An interesting feature of columns T, U and V is that it appears quite easy to read the true densities of these powders with an accuracy better than 0.01 g/cm^3. When doing this, we found no disagreement with data calculated from the composition of the powder (7). For this particular purpose a smaller powder sample might be preferred (in our case we still used 0.3 g) since the gradient is disturbed by the volume occupied by the particles. Care should also be taken to maintain a constant temperature.

When adequate precautions are taken and if necessary the density range is further reduced, it should be possible to determine the distribution of the true density between individual vacuole-free particles. Such a variation is to be expected due to compositional differences such as moisture content (related to particle size (8)) or lactose content (e.g. in precrystallized whey powder).

4 Conclusions

4.1 The method

The preparation of density gradient columns as shown in Fig. 1 requires normal laboratory equipment only. Care is needed in the construction and operation of the flow distributor. The non-linearity of the columns is a disadvantage that may be overcome, probably, by more sophisticated stirring.

A serious limitation of the method is encountered when the particles are partly soluble in the density liquid (egg powder, whole milk powder).

The qualitative visual analysis of certain columns (Section 3) may be followed by a more quantitative analysis (Section 2.2.7) if so desired. However in that case Verhoog's method (1) should be considered as well.

4.2 The results

There is a characteristic difference in the appearance of disc and pressure spray powders in the columns. Verhoog's conclusion (1) that disc spray powders contain a far smaller high density fraction than do pressure spray powders, is clearly confirmed (Fig. 3, 4 and 5). This difference, which vanishes when air-free atomization is applied (Fig. 3), is to be explained by the vacuole distribution (number and size of vacuoles per particle) rather than by the vacuole volume as such. Strong support for this view is derived from Fig. 5 (Section 3.4).

The method appears suitable for measuring the true density of powder material (Section 3.5).

Obviously the applicability of the method is not restricted to spray dried powders, nor to dairy products.

Samenvatting

J. G. P. Verhey en W. L. Lammers, *Een methode voor de bepaling van de deeltjesdichtheidsverdeling van verstuivingspoederdeeltjes*

In deze publikatie wordt de bereiding en het gebruik van dichtheidsgradientkolommen beschreven. Zulke kolommen blijken nuttig als hulpmiddel bij het bestuderen van de verdeling van de schijnbare dichtheid over individuele deeltjes. Verschillende toepassingen van de methode worden beschreven en met foto's geillustreerd. Daarbij blijkt dat de methode een nauwkeuriger inzicht geeft in de invloed van bepaalde omstandigheden tijdens het sproeidrogen en in algemene eigenschappen van bepaalde poeders.

Uiteraard is de methode in principe alleen geschikt voor poeders die vrijwel niet oplosbaar zijn in de kolom.

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