

**THE
BRITISH SOCIETY
OF RHEOLOGY**

BULLETIN — No. 4, 1963

Hon. Secretary :

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Mr. C. C. Mill, M.Sc., A.Inst.P., 19 Cray Avenue, Ashted, Surrey.

Mr. D. R. Reid, M.A., 18 Wellesley Road, Colchester, Essex.

Dr. J. H. C. Vernon, B.Sc., Ph.D., 106 Monkswood Avenue, Waltham Abbey, Essex.

Secretary's Report 1962-63

The year began with a very well attended meeting at the St. George Hotel, Harrogate, in September, on the "Rheology of Emulsions." About seventy members and others took part. Mr. P. Sherman arranged the programme, which included contributions by several distinguished persons from overseas. The papers will be published in book form by Pergamon Press. Administrative details of the meeting were undertaken by Mr. P. E. Knapp, who arranged visits to the floodlit Fountains Abbey and to the laboratories of the Research Department of I.C.I. Fibres Division. At the Annual General Meeting, the Society elected Dr. Roscoe President, in succession to Prof. Douglas. Mr. Knapp was elected to take over the editorship of the Bulletin, and Mr. R. J. Cole was welcomed as a newcomer to the Committee.

A joint meeting with the Society of Glass Technology was held in January on the subject of the "Viscoelastic Properties of Organic and Inorganic Glasses". Of the fifty persons attending this meeting in the Department of Glass Technology at Sheffield University, about one-third were members of the British Society of Rheology. We are indebted to the staff of the S.G.T. for most of the administration. The papers, again including a number from overseas visitors, have been published in "Physics and Chemistry of Glasses". Copies of the issue in which they appear have been supplied free to members attending the meeting, and at a reduced rate to about fifteen others who applied for them.

After much work by Dr. Saunders and his colleagues at the College of Aeronautics, Cranfield, the meeting on "Rheology of Metals" had to be cancelled through lack of support. Only fourteen applications were received, despite the attractive and varied programme which had been prepared. The Extraordinary General Meeting to consider the new Rules of the Society, a copy of the draft of which had been sent to all members, had to be postponed.

Attempts to arrange special travel facilities for members to attend the 4th International Congress of Rheology were unsuccessful, again through lack of support. About eight members travelled under Category Z, but otherwise only three expressed interest in a chartered flight. The Society will wish to record its appreciation of the work of Prof. Rivlin and his colleagues at Brown University in organising the 4th Congress.

The number of members of the Society has remained at roughly 350, plus forty whose subscriptions are overdue. Members not wishing to remain in the Society could save the Membership Secretary unnecessary work by advising him of their decision. All others can assist greatly by prompt payment of subscriptions. We have about fifty foreign members and over seventy in the Australian

Branches. To facilitate administration and to provide better service to members, an "Addressograph" machine was purchased for £50. (The Society also owns two portable typewriters.) A new list of members has been published.

The two Branches of the Society in Australia have been active during the year. In particular, the Victorian Branch has sent in some useful comments on the draft of the new Rules.

The Cambridge Rheology Club has also been active, thanks largely to the efforts of Dr. H. G. Muller. As Dr. Muller has now left the U.K. for a year, the secretaryship of the Club has been passed to Miss E. M. Nicholas.

Publication of the Bulletin and Rheology Abstracts has continued. Arrangements have been made for a number of articles of general rheological interest to be included in the future issues of the Bulletin. The Committee has given some thought to the fact that the price of Rheology Abstracts has been raised to £7 per volume of four issues, despite the fact that the Society provides the abstracts, and editing and indexing services. It must be pointed out, however, that the Society has always received copies for members at a much reduced rate. The index last year was compiled by Mr. R. J. Cole.

Early in the year a matter was raised by two members which may well serve to widen the scope and usefulness of the Society's activities. The Committee were urged to take note of the fact that there seems to be too little co-ordination of research in rheology, which is generally being undertaken by persons and organisations whose main interests lie elsewhere. As a result, progress in establishing the fundamentals of the subject is slow. Steps have therefore been taken to arrange a discussion of the matter at a general meeting of the Society, members' views having already been sought through a circular letter. The proposal will be put that an Exploratory Committee be set up to find out what can be done to promote research in rheology. All members have received a copy of the draft of the proposal, which was prepared by the President and Mr. Cole. We have here the prospect of the Society providing a co-ordinating function substantially beyond anything it has done in the past. Members are drawn from many fields of industrial and academic life; some of which are represented by very small minorities. It is likely that most meetings of the Society do not attract them, and such members may particularly welcome the setting up of an Exploratory Committee. They may well be able to assist it.

Steps have been taken during the year to establish representation of the Society on a number of British Standards Institution committees, including those on the viscosity of petroleum products, starch viscosity, physical testing of plastics, and particle density.

For the future programme beyond the present meeting at Keele, there is the possibility of a joint meeting with the Institute of Physics

in August on "Internal Friction"; and for the autumn meeting, we propose a variety of topics, including rheogoniometry, the teaching of rheology, and a session devoted to subjects which cannot normally find a place at one of the conferences. We had planned to hold a meeting at Easter on the "Rheology of Foodstuffs", in collaboration with the Foods Group of the Society of Chemical Industry. Extensive enquiries by Dr. Vernon have led to the conclusion that there is insufficient work available for publication at present.

This year the Secretary, Treasurer, and one Committee member (Dr. Saunders) are to retire by rotation, in accordance with the Rules. As I have already mentioned, the Society hopes to cater for rheological interests of many minority groups, and this is more likely to be achieved if the Officers and Committee are changed from time to time. The running of a society of this kind, without permanent staff or premises, is not necessarily done in the best possible way during the term of office of any one secretary, with whom the responsibility mainly lies. Fortunately, the Committee during the past four years has been continuously helpful and willing to share the administration, so that I can at least feel that the Society remains in working order. I shall always be grateful for this. Lastly, I should like to acknowledge the support the Society has received from British Nylon Spinners, through the interest in its work of the Research Manager, Dr. R. M. Lodge.

M. F. CULPIN, September, 1963.

Keele — September, 1963

Rheology of Clays and Fine Particle Suspensions

The meeting that the Committee had been planning for nearly three years took place at the University of Keele on September 25th–27th, 1963. Despite extensive enquiries by Mr. G. K. Jones, who dealt with the papers side of the meeting, only six contributors could be found. The subject is one where physics, chemistry and mathematics are seen to come together, and the papers were appreciated generally by the sixty or seventy participants, of whom a number had come to the meeting mainly for the other items of Society business. The papers were presented in the Physics Lecture Theatre, with excellent facilities, including space for Messrs. Ferranti and Messrs. Coulter Electronics to demonstrate instruments of rheological interest.

General administration of the meeting was by Mr. Hutton, whose arrangements worked extremely smoothly. We were fortunate with the weather, as the geography of the campus has its difficulties. The Union Building, the Refectory, the Physics Department and the residential blocks were all used at one time or another. As the distances do not really justify the use of automobile transport, and the

roadways hardly permit it (the Authorities definitely do not permit it!) one sympathises with the student body in bad weather. It so happened that on this occasion it was pleasant to have a few minutes walk to and from coffee, for example. A very good Conference Dinner was provided, at which the Society welcomed as guests Miss E. M. Rolfe, of the University, who had been most helpful at all stages of the organisation, Dr. Cooling, of the British National Society of Soil Mechanics and Foundation Engineering, and Prof. and Mrs. Springall, of the University.

The meeting included a visit to Messrs. Wedgwood's factory at Barlaston. It was a pleasant afternoon, but some members regretted not being shown the "dirty" end of the processes, where the rheologist is really at home. Mr. Hutton had in fact asked that we should see something of that, but the tour started where the clay had already been prepared for throwing or spreading, and took us then through the various stages of decorating and finishing.

Annual General Meeting

In addition to the routine items of business of an A.G.M. the meeting discussed the new draft Rules of the Society. The Rules, including amendments as set out below the Agenda for the A.G.M., were passed unanimously by thirty members of the Society.

Copies of the Secretary's Report for 1962-63, the Treasurer's Statement, and a list of Officers and Committee for 1963-64 appear elsewhere in the Bulletin. The meeting expressed appreciation of Prof. A. G. Ward's services as auditor of the accounts, and elected Prof. Ward to act in that capacity for another year.

The meeting was adjourned until after the discussion on the centralisation of research in rheology. After some amendment to the draft as sent to members, the resolution to set up an Exploratory Committee was then passed unanimously by twenty-nine members.

The Society is very grateful to Mr. R. H. Assheton, of Curwen, Carter and Evans, 1 Grays Inn Square, London, W.C.1, for legal advice and assistance in drawing up the new rules.

Centralisation of Research in Rheology

The topic was clearly a live one in the minds of those present. About ninety minutes were available for discussion and amongst those who contributed were: Prof. A. G. Ward, Dr. G. W. Scott Blair, Dr. A. Jobling, Mr. J. E. Roberts, Mr. R. A. Lammiman, Mr. R. H. Norman and Dr. G. H. Tattersall.

Views were divided as to whether centralisation in itself was desirable. One speaker thought that there should be an Institute of Rheology; another that there was scope for centralisation in work on

rheological measurements. Controversy arose too on whether or not rheology should be accepted as a distinct discipline in its own right. Should professors of rheology be appointed or is it enough that rheology be recognised as a branch of physics? It was pointed out that at present there are no chairs of rheology * but that Prof. Bingham was in fact a professor of rheology although nominally of another discipline. An approach similar to that adopted by the Institution of Chemical Engineers, viz., the setting up of fellowships (in rheology) was recommended, but another speaker emphasised that whilst the Society should encourage research it should neither direct nor inaugurate it.

At the resumed A.G.M. the following resolution was carried unanimously.

1. That this meeting empowers the Committee of the Society to set up an Exploratory Committee on Rheological Research to (a) consider the views on research expressed by members of the Society; (b) advise the Committee of the Society on action to be taken for the furtherance of rheological research, including those aspects detailed in the Appendix; and (c) advise the Committee of the Society on the establishment of a Standing Research Committee to assist in the implementation of any such action.
2. That the Exploratory Committee shall elect its own Chairman and may co-opt five additional members who need not be members of the Society.
3. The Secretary of the Society shall be a member of the Exploratory Committee and shall act as its Secretary.
4. That all members of the Society who have expressed views as to the organisation of rheological research in writing to the Secretary between October 1st, 1962, and August 1st, 1963, and the Officers and Committee of the Society be invited to serve on the Exploratory Committee.
5. That the Exploratory Committee shall present a final report to the Committee of the Society at the earliest possible date and in any case not later than June 30th, 1964.

APPENDIX: Matters for consideration of the Exploratory Committee under 1 (b).

- (i) Possibility of publication at appropriate intervals of a classified survey of general rheological research in progress,

* Dr. J. M. Alexander has been appointed to the chair of Engineering Plasticity at Imperial College and Dr. A. S. Lodge is Senior Lecturer in Rheology in the Faculty of Technology at Manchester University.

along the lines of the Survey of Chemical Engineering Research in Progress prepared by Warren Spring Laboratory. (The Chemical Engineer, 1962, No. 161, A59-82.)

- (ii) Gaps in present rheological knowledge and techniques.
- (iii) The institution of lively and realistic rheological research programmes in universities and technical colleges.
- (iv) The part Government Research Institutes could play in rheological research.
- (v) Locations where specific rheological research projects could be carried out.
- (vi) The provision of assistance to industry in formulating and implementing research programmes in which fundamental rheology is needed.
- (vii) The desirability or otherwise of a central laboratory for fundamental rheological research.
- (viii) Steps to draw the attention of appropriate organisations and institutions to the Society's efforts on behalf of rheological research.

[The first meeting of this Committee was held on November 14th.—Editor.]

ACCOUNTS FOR YEAR ENDING JUNE 30th, 1963

1961-62	INCOME	£	s.	d.
841	Balance on July 1st ...	748	3	5
351	Subscriptions ...	327	11	10
12	Interest P.O.S.B. a/c ...	12	19	0
4	Casual sales of Rheology Abstracts, etc. ...	3	19	3
5	Advertisements in Bulletin ...	16	0	0
		£1,108 13 6		

1961-62	EXPENDITURE	£	s.	d.
256	Printing and distribution of Bulletins and Abstracts ...	237	11	9
137	Committee and administrative expenses ...	180	11	6
53	Subsidy of meetings ...	7	13	5
26	Income Tax P.O.S.B. a/c ...	4	13	0
748	Balance June 30th ...	678	3	10
		£1,108 13 6		

COLIN C. MILL,
Hon. Treasurer.

ALAN G. WARD,
Hon. Auditor.

Branch News

The third Annual General Meeting of the Victorian Branch was held on July 31st. The following elections were made:

Chairman: Mr. B. D. Craven.

Treasurer: Mr. R. E. Price.

Secretary: Mr. K. R. Hall.

Committee: Mr. O. Delatycki, Prof. H. H. Dunkin, Dr. P. U. A. Grossman.

The formal part of the meeting was followed by a most interesting and entertaining lecture on "Rheology of Rubbers, Plastics and Proteins" which was given by Dr. P. Mason.

Future Meetings

A joint meeting of the Society with the Research Association of British Paint, Colour and Varnish Manufacturers on the "Rheology of Paints and Allied Products" will be held on Wednesday, 29th April, 1964. The meeting will be held at the Paint Research Station, Teddington.

An informal meeting on "Mixing and Flow of non-Newtonian and Heterogeneous Systems" is to be held at Swansea on 15th April, 1964, by the Institution of Chemical Engineers. Further enquiries should be made to Mr. J. M. Smith, Dept. of Chemical Engineering, University College of Swansea.

A meeting will be held in the Autumn with a dual theme. "Rheometry" and "Education in Rheology" are the topics but again the dates and place are not fixed.

The attention of members is called to the alteration of the date of the meeting on Polymer Physics mentioned in the previous Bulletin. This will now be held on April 1st-3rd, 1964, at the Royal Military College of Science, Shrivenham. Further information may be obtained from Dr. I. M. Ward, Research Department, I.C.I. Ltd., Fibres Division, Harrogate.

A note on the 4th International Congress on Rheology, at Brown University, August 26th-30th, 1963

In a traditional New England setting, Brown University provided the stage for the Congress which attracted participants, including some of the outstanding figures in Rheology, from many parts of the world.

The scientific programme was inaugurated by the welcoming speeches of Prof. Z. Bliss, Provost of Brown University and Prof. J. D. Ferry, President of the Society of Rheology, official hosts to the Congress. The programme was divided up into morning sessions of invited papers and afternoon sessions of invited and contributed papers, one complete morning being devoted to the presentation of

the Bingham Medal to Prof. C. A. Truesdell, by Prof. Ferry. Prof. Truesdell subsequently addressed the audience on "Rational Mechanics of deformation and flow", a summary of personal opinions on the state of the theory.

An analysis of the programme shows that a total of 176 papers were presented (one in title only), of which fifty-five were read to the Symposium of Biorheology, organised as a section of the Congress. Fifty-nine of the total were invited papers.

Due to the number of sessions running simultaneously in the afternoons (six Monday, nine Tuesday, eight Thursday and seven Friday), not more than a partial impression of the Congress could be formed and the comments of one person would by no means be an exhaustive account, neither are the following remarks a summary of the most important papers presented. However, it may be both useful and interesting to mention some of the areas covered.

Amongst the more striking lectures would surely be placed that delivered by H. Giesekus on "Some secondary flow phenomena in general elastico-viscous fluids", in which a colour film was shown of the flow patterns generated around a sphere and between a cone and plate (the cone apex angle being much smaller than that normally used in viscometry). Both pieces of apparatus were immersed in a bath of fluid and the flow patterns developed with varying speeds were visualised by the injection of dye. Very strong secondary flow developed in both cases and the struggle between centrifugal and elastic effects as the speed of rotation increased was clearly visible.

A related paper to the above was that by W. H. Hoffman entitled "Velocity field induced in a liquid by a rotating cone". In a Newtonian liquid sheared between a cone and plate it was found that for all angular velocities for which flow remained laminar, secondary flow existed for all the cone angles used.

The argument on the equality of p_{22} and p_{33} in the flow of polymer solutions is still a live one. Two papers were presented, one reporting experiments in cone and plate, parallel flat plate and capillary tube flow, from which it was found that the equality was true (to within better than 5 per cent accuracy in shear rate range 20 to 500 sec^{-1}). The other paper reported experiments using axial flow through an annulus, from which it was claimed that $p_{22} - p_{33}$ was positive and attained values of up to 30 per cent of the shear stress.

At the 1st International Congress on Rheology a phenomenon was described by B. A. Toms in which the friction pressure drop in the flow of dilute polymer solutions through tubes was less than that of the pure solvent. A paper by A. G. Fabula entitled "The Toms phenomenon in the turbulent flow of very dilute polymer solutions" described further work in this field, extending the previous work.

The criterion for the onset of turbulent flow in polymer solutions flowing through smooth round tubes in terms of a Reynolds number

was the subject of a paper by E. L. Kelly and J. G. Brodnyan, "The rheology of polyelectrolytes: (IV). The dependence of turbulence on polymer concentration". Some thought was given to the problem of the viscosity term in the Reynolds number. Use of any solution viscosity (such as the low rate of shear Newtonian viscosity for example) gave a critical Reynolds number which decreased with increasing concentration above a certain concentration, but use of the solvent viscosity led to an increasing critical Reynolds number.

In the flow of particle suspensions through tube, it was noted in a paper by H. L. Goldsmith and S. G. Mason, "Physical aspects of the flow of biological suspensions through tubes", that single small spheres in large tubes did not migrate radially, but that small liquid drops drifted towards the tube axis on their journey downstream. Another paper by G. Segre, "Necklace-like formations on the Poiseuille flow of a suspension of spheres" mentions that in the flow of dilute suspensions of rigid spherical particles not only did the particles tend to move to a region about two-thirds of the radius from the tube axis but that they also tended to form groups in the pattern of a necklace.

A paper was presented by the President of The British Society of Rheology, Dr. Roscoe, entitled "Measurements on the temperature variation of the rigidity of gels". A novel paper, "San movements in trees" by M. H. Zimmerman, described the two-way flow of fluids in tree trunks.

The ladies were well catered for by visits to local places of interest and there was a memorable gastronomical climax to the meeting—clambake at Mystic Seaport.

J. HARRIS,
Queen's College, Dundee.

Course in Rheology

It has at various times been suggested both inside and outside the Society that there should be full-time post-graduate facilities for the teaching of both the theoretical and applied aspects of Rheology. In consequence the Physics Department of Battersea College of Technology intends to offer a full-time post-graduate course in Rheology commencing in October, 1964. The course, which will be of one year's duration, will be open to suitable students of graduate status and will lead to the Post-graduate Diploma of the College (D.C.T. (Batt.)).

The course will consist of lectures, tutorials and laboratory work; in addition students will be expected to write a dissertation or carry out and report on a short research project.

Interested organisations and intending applicants are asked to communicate as soon as possible with Mr. R. W. Whorlow, who will be in general charge of the course, at the Physics Department, Battersea College of Technology, London, S.W.11.

Rheological measurements

Facilities will shortly be available in the Rheology Laboratory of the Civil and Mechanical Engineering Department of St. Andrew's University for the examination of material responses in a number of different flow geometries, notably, cone and plate, parallel plate, concentric cylinder and tube. Both normal and tangential stress measurements will be possible, except in the concentric cylinder apparatus, and both steady shearing and oscillatory motion is catered for.

Any member of the British Society of Rheology who may be interested in these facilities is invited to contact Dr. J. Harris, Queen's College, Dundee.

New Members

Elected September 25th

NAME AND ADDRESS

A. J. Chomppf,
Lab. for Physical Chemistry,
Technical University, Julianalaan 136,
Delft, The Netherlands.

A. F. Khattab,
Civil Engineering Dept.,
Battersea College of Technology,
London, S.W.11.

Z. Rigbi,
13 Adam Hachohen St., Haifa, Israel.

R. S. Marvin,
National Bureau of Standards,
Washington 25, D.C., U.S.A.

W. K. Gregson,
Ferranti Ltd., Moston, Manchester 10.

A. R. Pennell,
14 The Beeches, Greenacres,
Aylesford, Kent.

INTERESTS

Polymers and viscoelasticity.

Properties of clay by rotational viscometer and torsional plastometer.

Viscoelasticity.

Polymer Physics.

Rotational viscometers.

Clay suspensions, paper coating mixes. Rotational and extrusion viscometry.

Elected September 27th

A. F. Lanham,
Reed Paper Group Ltd.,
Research Centre, Aylesford, Kent.

A. D. Myers,
37 Leamington Road, London, W.11.

E. K. Obiakor,
Dept. of Mining,
University of Nottingham.

F. Evans,
D.S.I.R., Warren Spring Laboratory,
Stevenage, Hertfordshire.

R. L. Whitmore,
Dept. of Mining Engineering,
University of Nottingham.

Clay suspensions, paper coating materials, adhesives.

Plastic clays, suspension of clay in water.

Suspensions of powder in liquids, rotational viscometry.

Non-Newtonian fluids in chemical process equipment.

Rheology of dispersed and flocculated aqueous suspensions of powders. Biorheology.

Dough Rheology and some Problems of Bread-making

by S. J. CORNFORD

This article is a review of some ways in which empirical measurements of the mechanical properties of wheat flour doughs for bread-making have recently helped to further the understanding of some rather difficult and longstanding problems of the industry. It is intended to be of interest to those whose work lies in other fields, and so no attempt has been made to review the subject completely.

It should be emphasised that the character of the work described is international, and many organisations have taken part in it.

The background to the problems

The rheological properties of dough for bread-making have been studied for a long time on account of their obvious connection with the volume and texture of the finished loaf. The essential ingredients are flour, water, yeast and salt, and these are mixed to form a dough with visco-elastic properties, which is fermented in bulk for a period of some hours, usually three hours, before dividing into pieces for baking.

The volume of the finished loaf depends on two main factors. (1) There must be an adequate supply of carbon dioxide gas during the period when the dough is rising in the tin and in the early stages of baking in the oven. This gas comes from fermentation of sugars by the yeast and needs the correct proportion of both. (2) The mechanical properties of the dough must be correct to allow its expansion without loss of gas or breakdown of the fine cells. These properties are determined by the condition of the rubber-like gluten, which is formed when the protein part of the flour absorbs water, and in which the starch granules are embedded.

When the time of bulk fermentation of the dough is varied over a period of some hours, with appropriate variations in the recipe to ensure adequate gas production by the yeast, it is found that the best bread, with largest volume, and finest texture, can only be made over a fairly narrow range of fermentation times of about one hour, when the dough is said to be "ripe" or ready for bread-making. At shorter times, the loaf is smaller, cell walls are thicker and the crumb tougher. At longer times volume is also reduced but the texture is characterised by large holes resulting from cell breakdown.

The effect of improvers

When flour is freshly milled, or more particularly when the best quality flour of high protein content is used, the best fermentation time is inconveniently long, and it is the practice to treat the flour with a few parts per million of certain oxidising agents which are known as "improvers". Chlorine dioxide and potassium bromate are commonly used for this purpose, while ammonium persulphate,

ascorbic acid, and potassium iodate* are used to a lesser extent. These substances have the effect of reducing the fermentation time required to obtain the best bread from a given flour. In England, a bulk fermentation time of three hours is very commonly given, and the level of flour treatment is adjusted to suit this.

The mode of action of these improvers has been studied for a long time, and the subject is of particular interest to rheologists because their effect can be followed by the change which occurs in the rheological properties of doughs to which they have been added.

In order to explain how this is done it is again necessary to digress briefly to describe some essential features of bread-making. When the bulk dough is divided into loaf-size pieces, these are rounded into balls and allowed to rest for about ten minutes to recover from the effects of the action of dividing. The dough pieces are then moulded, a process which stretches and folds the dough as well as shapes it, and placed in tins. The dough must not rise entirely in the oven, but partly beforehand in the tins, a process known as "proof".

Rheological measurements

The rheological properties of the dough are usually measured by means of an empirical test on a machine which grips a prepared specimen of dough, extends it at a constant rate, and records the force required to perform the elongation.

If pieces of dough were to be cut from a bulk dough and tested without further preparation, it would be found that the dough softens gradually with time. This, however, is not the usual method of test and would not be found to correspond to the bread-making capabilities of the dough. When the dough samples are moulded in a similar manner to the dough pieces for bread-making, the dough becomes very resistant to stretching and very large forces are required. When the dough is rested after moulding, the stretching force gradually decreases to a limiting value over a period of about an hour. It is customary to test after a fixed rest period of about 25 minutes after moulding the test piece. When this is done, the effect of fermentation is shown as a gradual increase in the stretching force and a gradual decrease in the elongation before breakage occurs.

When different flours, with different protein contents, and which may need different proportions of water in the dough are compared, it is found that the ratio of maximum elongation to maximum stretching force is a good measure of dough ripeness, a fairly narrow range of values indicating the correct fermentation time for production of the best bread. The effect of flour improvers on the test

* Potassium iodate will not be permitted in the U.K. after September, 1964.

values corresponds under these conditions with their effect on the finished loaf and the reduction in optimum fermentation time can be correctly predicted from the dough properties. Such tests are carried out as a routine to help the miller and baker.

On the other hand, if the dough is not moulded or is tested in a fully relaxed condition, then no effect on dough properties is observed when improvers are added. Their effect is only observed as a change in the properties of the dough, as indeed in the finished loaf, after a process of stretching and folding the dough has taken place.¹ It is therefore necessary to test the material in an unstable, highly orientated condition, where its properties are necessarily anisotropic, in order to assess those factors which are of industrial significance. These empirical tests have been made to yield a great deal of information, while attempts at more fundamental measurements have not generally been so useful.

Study of improver action

The action of improvers, such as potassium bromate, can be characterised more precisely in terms of their effect on the rheological properties of the dough by plotting the force required for a convenient constant extension against the time following moulding. The force decreases with time to a limiting value and the graph is a hyperbola. This can be characterised by the semi-axis constant and the asymptotic force after a theoretically infinite time.² It has been found that the semi-axis constant gives a linear plot against potassium bromate concentration for a given reaction time after mixing the dough, and consequently the value for a control dough without additive can be subtracted to give a measure of the effect of the improver. It has been found in the case of potassium bromate that the slope of the linear plot is increased with an increase in the reaction time and, in fact, a linear plot is obtained of the semi-axis constant for the bromate effect against its reaction time in the dough.³ An increase in the semi-axis constant corresponds to a slower relaxation of the effects of moulding on the dough.

Parallel to these rheological measurements chemical studies showed that the disappearance of potassium bromate in the dough also gave a linear plot against reaction time.

The link with sulphydryl groups

The next step in the chain of evidence relating to the effect of improvers in dough would be to show with what part of the dough they react. It had for a long time been suspected that the sulphur-containing amino acids in the flour protein were the reactive groups involved in reduction and oxidation reactions. These are the amino acids cysteine, cystine and methionine.⁴ The reaction envisaged was that pairs of sulphydryl groups $-SH$, within the protein complex

would react in the presence of an oxidising agent to form a disulphide cross-linkage $-S-S-$.

Unfortunately the proportion of sulphydryl groups in dough in relation to disulphide groups was too small for accurate chemical studies of the effect of oxidising agents, although in substances where there was a high concentration of sulphydryl groups, e.g., glutathione and cysteine, the rate of oxidation of sulphydryl groups by iodate, bromate, chlorate and persulphate was shown to parallel closely their relative rates of reaction as flour improvers.⁵

A possible mechanism

The approach was therefore indirect, and again rheological measurements played a significant role.⁶ It was difficult to see how the marked changes in dough properties which occur could be accounted for by a relatively small increase in the proportion of disulphide cross-linkages which would be caused by oxidation of the available sulphydryl groups. The most likely way in which a change in the relatively small proportion of sulphydryl groups could exert a controlling influence on the dough properties would be by exchange reactions with disulphide groups. If exchange reactions could take place between sulphydryl and disulphide groups, it would be possible for a relatively small proportion of the former to control the rate of relaxation of internal stresses in the dough by the breaking and re-formation of disulphide cross-linkages.⁵ The effect of flour improvers is to inhibit the relaxation of the effects of moulding the dough, and this might be explained by the inhibition of the breaking and re-formation of disulphide cross-linkages in the dough.

Some further evidence

The evidence for this type of reaction is not conclusive, but it has been shown that the effect of blocking sulphydryl groups by reacting them with agents such as N-ethylmaleimide or p-chloromercuribenzoate has a similar effect on the rheological properties of dough to the addition of improvers. Thus the action of improvers is conclusively linked with the loss of sulphydryl groups in the dough.^{7, 8}

If the proportion of sulphydryl groups is increased by the addition of cysteine, the relaxation of the effects of moulding the dough takes place more quickly than in a control dough.⁷ Reaction of dough with the reducing agents thioglycollic acid, cysteine hydrochloride, reduced glutathione, thiolated gelatin, sodium bisulphite and sodium borohydride, all of which increase the proportion of sulphydryl groups in the dough, before incorporation of potassium bromate increases the latter's reaction rate in proportion to the amount of reducing agent added. This is consistent with the bromate ion reacting with an increased proportion of sulphydryl groups.⁹

If the relaxation of molecular orientation due to moulding is controlled by the concentration of sulphydryl groups, which promote

changes in molecular configuration by breaking and re-forming disulphide cross-linkages, then the measurement of fundamental rheological parameters becomes difficult because the material will be changing its nature during the course of a test, and this may explain some of the difficulties of interpretation which have been met in attempting to make this type of measurement.

Problems remain, but the mechanism of improver action is better understood than it was a few years ago. Much has been omitted from this article, particularly the advances in chemical techniques, but some of the ways in which rheological studies have helped in these investigations have been indicated.

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