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A REVIEW OF RAW WOOL CARBONISING

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1. INTRODUCTION

Most greasy wools contain vegetable matter (VM) acquired by the sheep during grazing. This can comprise a variety of different vegetable matter types such as burrs, seeds, twigs, leaves and straw[1-12]. During pre-processing of wool i.e. shearing, skirting, classing, blending and packing, very little, if any, of this vegetable matter is eliminated. Some of the vegetable matter is removed during mechanical opening and dedusting prior to scouring, but the bulk is removed during mechanical processes subsequent to scouring. The presence of relatively large amounts of VM on the wool after scouring, however, can lead to difficulties in its removal and to a variety of problems during the manufacturing processes. In severe cases, damage to card clothing and combs can occur, yarn breakage can increase during spinning and speckiness can be observed in dyed fabrics[11].

While mechanical means is satisfactory for VM removal in most cases, particularly when the level of VM is medium to low, there are cases where (1) the VM content is higher than that which can be accommodated by or (2) it is of such a type that it cannot be accommodated by the available processing machinery or (3) a totally VM-free product is required. In such instances, a chemical treatment known as carbonising is required[13,14]. Vegetable matter is also known to be more prevalent in certain classes of wools, such as bellies and lox and, therefore, such types are more frequently carbonised than others.

Ward[15] surveyed the early-stage processing of wool worldwide and reported that in 1983 most of the world's carbonising of greasy wools took place in Australia and some in South Africa and the Asian region. Apart from this, there are a few major commission-carbonising mills operating elsewhere.

The current statistics from the Commonwealth Secretariat[16] indicate a carbonised wool production in 1984 of 39 388 tonnes clean, about 10% of the scoured wool production in the major wool processing countries excluding Eastern Europe. In spite of this significant carbonised wool production worldwide, no up-to-date review of this field is available at present, and, therefore, it was decided to carry out a review on this topic. The aim of this review is to survey carbonising techniques and developments in carbonising technology over the last 60 years.

2. CONVENTIONAL CARBONISING OF WOOL

The conventional carbonising process comprises five main stages, i.e. (1)

scouring, (2) acidising, (3) drying and baking, (4) burr crushing and dedusting and (5) neutralising.

2.1 SCOURING

The scouring of wool has been extensively researched and the literature on the topic has been reviewed by several authors[17-20]. However, literature on the effect of scouring conditions on carbonising of wool has been confined to only a limited number of publications[21-24] Pressley[21] found that the source of vegetable matter had a much greater influence on the acid uptake during acidising than the actual scouring process while Malek and co-workers[22] found, for one type of wool, a high dependency of the quality of the carbonised wool on the type of detergent (anionic, cationic or nonionic) and scouring machine (pilot or industrial scale) used.

2.2 ACIDISING

The acidising operation is carried out in an acidising bowl. Sulphuric acid is by far the most commonly used reagent for carbonising. Most work in this area has been directed towards studies on the treatment of wool with sulphuric acid to produce maximum acid penetration of the vegetable matter, while keeping the acid concentration of the fibre at a safe level from the point of view of possible damage during the subsequent stages of carbonising.

2.2.1 Acidising Conditions and their Effect on Acid Uptake

A number of alternative procedures for acidising under industrial conditions have been suggested[25-37]. Mizell and co-workers[25-27] recommended immersion of wool for 15 to 60 seconds in a cold acid solution (10 to 16°C) containing a relatively high concentration of sulphuric acid (7 to 7,5%). Alternatively, they suggested the use of a milder warm acid solution (acid concentration 4,5 to 6,5% and temperature 32 to 38°C) for a longer immersion period (2 to 5 min.). In the first case, the acid content of the squeezed wool was below the value of 5,5%[25,26] (a level which they regarded as critical as far as damage to wool was concerned) and that of the burrs around 2,8%. In the second case, the acid content of the squeezed wool exceeded the "critical" value, reaching levels of around 7,5%[25,26]. Although Mizell and co-workers[25,26] claimed that short immersion times combined with relatively strong acid solutions (7%) led to successful carbonising of the vegetable matter (with acid content of the fibre below "critical" levels), experiments carried out at the University of New South Wales by Nossar and co-workers[28] showed that considerable chemical damage to the fibre could occur when using relatively high concentrations of acid e.g. 7%. The reason for this fibre damage was due to the non-uniform

distribution of the acid on the fibre, which led to its concentration exceeding the safe limits, thus attacking the fibre and causing damage in localised areas[28]. Patel[29] found that minimal damage to the fibre and a high degree of carbonising of the burrs were obtained with a relatively mild sulphuric acid treatment (4%) at a temperature of 30 to 36°C, coupled with long wool immersion times (5 to 10 min.).

The effect of acidising conditions on the uptake of acid by wool and burrs has been investigated by a large number of workers[5,6,21,25,26,29,34,36,38—45]. Pressley[21] conducted a laboratory investigation into the uptake of sulphuric acid by wool and by the common trefoil burr Medicago minima) and found that small differences in acid concentration or squeeze roller efficiency had a minor effect on acid uptake by wool. Pressley[21] also found that the origin of the burr had a much greater influence on acid uptake by burrs than increasing the acid concentration or the time of immersion in the acid bowl. Satisfactory carbonising of this trefoil burr was achieved for a burr acid content of around 6% but no carbonising occurred at an acid content of about 3%.

Along similar lines, Jones[38] carried out a comparative study of the rate of sulphuric acid absorption by pre-rinsed and squeezed burrs (or wet burrs) and dry burrs of the Medicago minima type. Jones[38] found that the acid absorption rate was slower and the acid equilibrium level was slightly lower for dry burrs than for wet burrs (the difference in equilibrium level becoming insignificant after 8 minutes immersion time). However, an increase in temperature of the acid medium increased the absorption of acid by dry burrs[38].

Mizell and co-workers[25, 26] found that the minimum acid levels for adequate carbonising of burrs depended on the type of burr, varying from 2,5% for shives to 3% for spiral and sand burrs and to 4% for cockle and green burrs.

Veldsman[39] suggested that immersion time in the acid bowl should be as brief as possible, not exceeding one minute, since burrs absorbed their maximum amount of acid within the first minute, while wool required two to three minutes to achieve this. He also pointed out that the temperature of the acid bath played a significant role on acid uptake. Wool was reported to absorb less acid at 10°C than at 32°C, while burrs absorbed the same amount at both temperatures. Therefore, the lowest temperature was preferable.

2.2.2 Use of Auxiliaries in the Acidising Bowl

Concerted efforts were made during the 1920's and the 1930's to find chemicals which could assist in the penetration of the acid into the burr. The ensuing research resulted in a number of patents being taken out[46—50]. The first patents[46,47] referred to the addition of an aromatic acid, i.e. p-toluene sulphonic acid or benzene sulphuric acids or one of its salts to the acid bowl (which allowed

the use of a lower sulphuric acid concentration). Later patents[48—50]referred to the use of aryl-alkyl sulphonic acid and similar chemical compounds as auxiliaries in the acid bowl.

Research work on the addition of wetting agents to the acidising liquor started in the 1950's. An overwhelming number of authors[5,25,26,44,51—60]concluded that wetting agents provided some degree of protection to the fibre, reducing loss of fibre strength during carbonising. Jones[38], however, found that addition of these agents to the acidising liquor had only a minor effect, if any, on the rate of sulphuric acid absorption by wet and dry burrs of Medicago minima.

The effect of the type of surface-active or wetting agent on carbonised wool was investigated in some depth by several workers[5,44,51,52,54,55]. Crewther[51] found that a number of surface-active agents were effective in providing adequate protection. Further studies carried out by Crewther and Pressley[54] showed that nonionic agents based on polypropylene oxide provided little protection to the fibre even at the highest concentrations tested, whereas nonionic agents containing an alkyl or aryl hydrocarbon group were generally effective. With the latter types of wetting agents, the required addition depended upon the length of the polyethylene oxide chain. Anionic agents were found to be ineffective at low concentrations; cationic agents were comparable in their effect to nonionic agents.

The results of a later study[5] showed that polyethylene-oxide-based nonionic agents were only effective if they had at least 10 to 15 polyethylene oxide groups in the polyethylene oxide chain and a sufficiently long hydrocarbon chain (16 to 18 carbon atoms). It was found that addition of this type of wetting agent to the acidising liquor produced an increase in the carbonising yield due to a reduction in the loss of broken fibre in the willey dust and a reduction in the protein loss[5] due to fibre dissolution in the neutralising bowl.

In general, the results of this study[5] were in agreement with findings by Crewther and Pressley[52,53,55], who found that the addition of surface-active agents to the acid bowl during carbonising produced (1) an increase in yield of carbonised wool and an increase in yarn strength on spinning on the woollen system[52,55], (2) an improved gilling and combing performance on the worsted system[52] and (3) an improvement in the colour and strength of the carbonised wool[53].

Sadhir and co-workers[44] found that 0,2% sodium lauryl sulphate could be used in the acid bowl to minimise damage to wool while attaining a satisfactory removal of burrs (this should be compared to the levels of 0,01 to 0,02% recommended by Mizell and co-workers[25—27] for nonionic surfactants). The residual burr content of the carbonised wool was found to vary in a very narrow range with the variation in detergent addition to the sulphuric acid solution[44].

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Various authors have attempted to explain the mechanism by which surface-active or wetting agents provide protection to the fibre. Crewther and Pressley[55] believed that this was due to a reduction in the level of embrittlement of the wool when wetting agents were present in the acidising liquor. Mizell and co-workers[25,26,56] claimed that wetting agents did not serve as direct protection to the fibre during acidising but that they had an indirect beneficial effect on the tensile strength of the wool, insofar as their presence in the acid bowl produced a reduction in the moisture content (and therefore the acid content) of the acidised wool before and after the squeezing stage. Nossar and co-workers[57–60] used fluorescent stains as sensitive qualitative indicators of weak spots caused by acid damage to wool fibre in an attempt to establish the role of wetting agents in the process. They suggested that the protective action produced by these agents could be a function of the improved spreading of acid droplets (or evenness of acid spreading) on the fibre during the subsequent drying stage, resulting in a more uniform distribution of acid on the fibre[59].

2.2.3 Moisture Content of Acidised Wool

A number of workers[51-54, 61–66] investigated in depth the effect of moisture content of acidised wool on carbonising and agreed that the presence of excessive amounts of water (over 60% moisture content) in the acidised wool could cause deterioration in tensile strength and alkali solubility of the fibre, although they disagreed as to the extent to which this damage could occur (see section 2.3.1).

Brach[67] investigated the removal of water and acid from acidised burry wool by means of a centrifugal extractor. Brach claimed that this type of extractor greatly reduced the moisture content of the wool and thus reduced the loss in fibre strength without considerably affecting the moisture content of the burrs. To avoid discontinuity in the carbonising process, however, the use of a continuous horizontal decanter centrifuge was suggested[67].

Workers in Belgium[67–70] introduced the concept of a continuous hydroextraction stage prior to drying and baking. Previously, centrifugal hydroextraction had suffered from the disadvantage that it required a break in the carbonising cycle. However, the appearance on the market of continuous hydroextractors with horizontal pushers motivated research in this area. Using wetting agents and a continuous hydroextraction time of 2 to 3 minutes, acidified wool with an average moisture content of about 47% and an acid content of about 7% was obtained. Under the same conditions, burrs had, on average, a moisture content of about 51% and an acid content of about 5%[70].

2.3 DRYING AND BAKING

The drying stage can be considered as one of the most critical phases of

the entire carbonising process. During this stage a large portion of the moisture in wool is evaporated at temperatures below 70°C, leaving concentrated sulphuric acid on the fibre and burrs. Under the influence of the acid, the vegetable matter burr (of cellulosic origin) is chemically attacked. However, it is also at this very stage that the wool fibre can suffer lasting damage if due care is not exercised.

The baking stage, which takes place in a second dryer called "Baker" or "Carboniser", involves heating of the wool to temperatures above 100°C (normally 120 to 130°C). Here, under the influence of the concentrated sulphuric acid, the burr becomes brittle and charred. The charred substance (mainly carbon) generated in this manner can then be removed from the wool in the subsequent stage by mechanical crushing and dedusting.

2.3.1 Fibre Damage During Drying and Baking

Harris and co-workers[64] investigated the effect of acid concentration and immersion time on the amount of damage sustained by wool fibres and found that in concentrated sulphuric acid (above a concentration of 80% at room temperature) or during the drying and baking stages of the carbonising process, sulphamic acid is formed. This reaction was found to be irreversible and resulted in permanent damage to the wool, as evidenced by changes in its dyeing properties[71].

While most workers in the field of carbonising agreed on the causes for damage to the fibre being those found by Harris and co-workers[64], they disagreed on whether most of the damage occurred during the drying or during the baking stage. Harris[72], on the one hand, suggested that fibre damage occurred during the first few minutes of baking, after which there was no further fibre breakdown. Bauer[73], on the other hand, claimed that fibre damage occurred also during the drying stage and was, in fact, a function of drying time.

Crewther[61] found during laboratory studies that when wool was treated with sulphuric acid and heated in a closed vessel to 100-105°C, tensile strength decreased slowly and alkali solubility increased markedly with an increase in treatment time. However, when the acid-containing wool was dehydrated before heating, there was a rapid decrease in tensile strength with little change in alkali solubility[52,54,65]. Crewther and Pressley[52,54,65] concluded that any large increase in alkali solubility which occurred during the carbonising process was almost certainly attributable to excessive heating before drying was complete[52].

Wibaux and co-workers[67] disagreed with these findings[52,54,65] and claimed that (1) when carbonising under anhydrous conditions, the loss in fibre strength was not as great as that found by Crewther and Pressley[54], (2) that under industrial condition, the presence of excessive amounts of water during heating caused a significant loss in tensile strength and (3) that alkali-solubility alone could not be considered as a sufficient test for damage in carbonising.

2.3.2 Effect of Acidising Conditions on the Wool during Drying and Baking

Mizell and co-workers[25,26] found that when the acid content of the wool was kept at about 5% or less during acidising, the wool could be dried, or dried and baked (at any temperature up to 150°C) without reducing the tensile strength of the fibre. When the acid content was above 5,5% the wool required drying at a low temperature (65°C or less) to a moisture content below 15% before it was baked. Further experiments indicated that when the wool contained 10% sulphuric acid, significant strength losses occurred even when it was dried at 20°C[25,26].

Nossar and co-workers[28,57,60] investigated the role of surfactants on the wool during drying and found that these increased the rate of drying owing to the better spreading of the acid solution on the fibre[57]. Furthermore, they found that an increase in the time interval between acidising and drying allowed a re-distribution of acid on the wool fibre[60]. It was suggested[28] that sufficient time for complete acid diffusion into the fibre could be provided by using a large feed hopper for acidified and squeezed wool, thus allowing for an adequate time delay to be obtained before it was fed into the dryer and baking oven.

2.3.3 Drying and Baking Conditions

A variety of authors[25,26,74-90] investigated the drying and baking stages of the carbonising process. Kitazawa[76] carried out an investigation using a five-stage drying unit and found that wool was almost completely dry after the second stage and then became carbonised in the next three stages. Temperatures within the dryer fluctuated between 100 and 120°C, depending on the location of the point of measurement. Complete carbonising of trefoil burr was obtained during these trials. A later publication[77] claimed, on basis of industrial experience, that best results were obtained when the wool was treated in two stages, i.e. (1) drying at moderate temperatures to a low moisture content of around 3 to 4%, and (2) subsequent baking at somewhat higher temperatures. According to this publication[77], such a system had the additional advantage that the wool was re-distributed after the initial drying stage by a hopper feeder supplying the baking section, so that all parts of the wool and the burrs were exposed to the drying air.

Robinet and Bielen[74,75] found that it was important to dry the wool at relatively low temperatures (50 to 60°C) in order to avoid hydrolysis of the keratin, which would result in the deterioration of mechanical properties and a change in chemical characteristics of the wool. As far as the baking stage was concerned, Robinet and Bielen[76] suggested that a temperature of 105 to 110°C would ensure the degradation of the cellulosic residues on the fibre.

Mizell and co-workers[25,26] studied the drying and baking processes in

some detail. They found a direct relationship between the loss of fibre strength and drying temperature. As far as the effect of drying time was concerned, the tensile strength of the acid-treated wool decreased only while the fibre was drying. After the wool was dry, further residence time in the dryer did not affect the tensile strength. Mizell and co-workers[25,26] also found that the optimum baking temperature and baking time depended upon a number of factors such as the openness of the wool during heating, the thickness of the layer of wool, the air velocity in the baking oven and the amount of acid on the vegetable matter. They concluded that wool should be dried at a relatively low temperature (65° C or lower), depending on the fineness of the wool and its actual acid content. A high air velocity was recommended for drying, in order to yield a moisture content below 15%. A 3-minute baking period at an air temperature of about 150°C and air linear velocity of about 2m/sec was further recommended. The authors claimed that, under these conditions, complete carbonising of the burrs could be obtained with a minimum descolouration of the wool and little, if any, loss in tensile strength[25,26]. Veldsman[39] recommended that (1) the moisture content of the wool entering the baking unit should preferably not exceed 10%, (2) baking should be carried out at a temperature not in excess of 130° C and (3) the thickness of the wool layer during baking should not exceed 45 mm .

Patel and Ramamurthy[78, 79] investigated Indian wools with a relatively high burr content and also found that satisfactory carbonising was achieved at a baking temperature of 130° C. The authors confirmed that drying was the critical stage of carbonising[80] and that as far as baking was concerned, yellowing of the wool only occurred at a temperature of 160° C[81].

2.4 BURR CRUSHING AND DEDUSTING

Once the burr-containing wool has been dried and baked (i.e. carbonised), it is passed through a burr-crusher which pulverises the charred vegetable matter by means of a series of heavy crush rollers, mounted on roller bearings. The dust resulting from the crushing is removed in a deduster or willeying machine, which has an adjustable speed to cater for different types of wool and incorporates specially designed hoppers which can be connected to a dust extraction unit. For maximum efficiency, two burr-crushers and dedusters are normally installed in tandem.

Early published literature on burr crushing[91,92] deals with developments in the design of continuous crushers. These machines were designed to perform both functions, namely burr crushing and dedusting, and consisted of two tandem units, each equipped with four sets of metal rollers, the bottom ones being knurled. Vibration was reported to have been practically eliminated and both units were enclosed and equipped with large capacity fans located directly beneath to ensure complete exhaustion of dust. In later years[78, 79], the two

functions i.e. burr crushing and dedusting were separated. This was done in order to improve the efficiency of burr removal, the crushing of the carbonised burrs being carried out in the burr crusher and dedusting (or elimination of residual dust from the fibre), in the deduster.

Research in the mid-1960's in Australia[6] showed that the Willey dust (i.e. the debris removed from the wool fed into the rotating cage of the deduster) contained an appreciable amount of fibre, which represented a considerable fibre loss factor to be considered when analysing the carbonising process. This finding was confirmed later by Bhan[41], who reported that, in spite of the considerable amount of research that had been carried out on carbonising, it was not uncommon to find considerable loss in mass and tensile strength of the fibre during the mechanical and neutralising stages of carbonising[93].

Katz and co-workers[94] found that burr crushing could cause considerable fibre damage. Nossar and Chaikin[28] found that such damage occurred when fibres became trapped between the burrs and the fluted (or knurled) rollers of the burr-crushers. Chaikin and Collins[95] reported that this damage was due to the rubbing effect produced by the top and bottom rollers moving at different speeds. This effect was considered to be essential when crushing thick layers of wool but this speed differential was considered to be unnecessary if a sufficiently thin layer was processed[95]. Effective crushing was obtained when both rollers were running at the same speed, which was only possible when a sufficiently thin layer of wool was fed into the machine[28].

2.5 NEUTRALISING

The wool leaving the dedusting unit has a relatively high acid content which can cause damage to the fibre if it is not properly neutralised. The neutralising sequence normally comprises a combination of the following stages: (1) treatment with an alkali such as soda-ash, (2) mild scouring, (3) rinsing and (4) final drying of the carbonised product.

2.5.1 Conventional Soda-Ash Neutralising

The neutralising operation is usually carried out in a machine comprising three to four bowls, the first or first two for neutralising with soda-ash to destroy residual acid and the remaining two bowls for a mild scour and rinse and for washing off any dust not removed by the deduster. During the first half of this century, it was common practice to add soap to the neutralising bowl or neutralising bowls[96,97] but this practice has since been replaced with the addition of nonionic surface-active agents. The final drying of the carbonised, neutralised and rinsed wool is carried out in a suitable dryer, similar to that used for drying of scoured wool.

In the mid-1950's, Kitazawa[76] found the efficient neutralising could be obtained by using two soda-ash bowls in succession, the first charged and maintained at an alkali concentration of 0,3% and the second at a level of 0,4%, together with a surface-active agent. Recommended residence times for the wool were about 3 and 2 minutes for the two bowls, respectively.

Harker[98] carried out an in-depth investigation into neutralising and found that the concentration of soda-ash, time of immersion of wool (or residence time in the bowl) and the liquor-to-fibre ratio were the neutralising-rate determining factors. Since the volume of the bowl was normally fixed and the time of immersion could not be altered significantly, the soda-ash concentration and the wool throughput were found to be main variables (the temperature was found to have only a marginal effect). For instance, carbonised wool with an acid content of 4 to 10%, neutralised in a 0,5% soda-ash liquor was found to yield a satisfactory and virtually constant residual acid content for liquor-to-fibre ratios above 50:1. However, the neutralising efficiency was found to be unsatisfactory for a soda-ash concentration of 0,1%. Also, increased times of immersion gave, in general, a lower residual acidity with a minimum value being reached after 20 minutes. Harker[98] also reported that the pH of the neutralising bowl was found to decrease slowly due to the formation of sodium bicarbonate but, provided the concentration of soda-ash was maintained and the wool throughput was not excessive, this did not affect the amount of alkali available for neutralising.

Another investigation carried out in Belgium[70] revealed that the amounts of soda-ash required to maintain the pH of the bath exceeded that required theoretically, due to conversion of sodium carbonate into bicarbonate. As a result of this, an attempt was made to add only moderate amounts of carbonate to the second neutralising bowl and it was found that, as long as the concentration of bicarbonate was maintained at a level of about 1%, neutralising of wool continued at a reasonable rate.

Hille and Zahn[99] investigated the chemical aspects of the neutralising process. They recommended that carbonised wool be completely neutralised and, furthermore, be brought to a slightly alkaline pH value of 8,6. This would prevent further chemical degradation of the wool after neutralising.

Nossar and Chaikin[28] found that wool suffered the greater degree of entanglement during the acidising and neutralising stages of carbonising and this could cause fibre breakage during subsequent mechanical processing. In their view, fibre entanglement could be greatly reduced by constraining the fibre movement whilst the wool was immersed in liquors and by opening the wool layer at frequent intervals, i.e. after each squeezing and between each of the process stages.

2.5.2 Alternative Schemes for Soda-Ash Neutralising

During the 1960's Bhan[41] reported on the use of a modified scheme for neutralising in India. Wool was first rinsed in cold water (this operation removed at least 50% of the acid from the fibre), thereafter it was treated in a weak soda-ash bath and finally rinsed in water again. However, this neutralising sequence seldom gave satisfactory results. Up to 2% residual sulphuric acid was reported[41] to be present on the carbonised wool after neutralising.

Along similar lines, Tobisch[100] described a typical neutralising sequence in the Hungarian carbonising industry. Carbonised wool was rinsed with cold water (10 to 15°C) in the first bowl, treated with soda-ash at a pH value of 8 and a temperature of 38°C in the second, treated with soda-ash again at a pH value of 7,5 and a temperature of 40°C in the third and finally rinsed with cold water (10 to 15°C) in the fourth. A fifth bowl was deemed necessary at times in order to bleach the wool, although careful monitoring of the neutralising process obviated the need for bleaching. Final drying was reported[100] to be carried out in a suction-drum type dryer.

Knott and Zahn[101,102] found that pretreatment of carbonised wool with isopropanol before immersion in a soda-ash solution improved the degree of whiteness of the wool and increased the rate of neutralising. Other alcohols such as ethanol were also highly effective but only at high concentrations. Anionic and nonionic surfactants also promoted the removal of acid from wool. For instance, in the homologous sodium-alkyl-sulphate series, the efficiency of the detergent increased with an increase in chain length. The hexyl derivatives were found to be completely ineffective[101].

2.5.3 Use of Alternative Neutralising Agents

Robinet and Bielen[103] studied several alternative neutralising agents for wool carbonised with sulphuric acid, namely sodium carbonate, sodium bicarbonate, potassium carbonate and ammonium carbonate, as well as other modifications to the conventional neutralising process. They found that the residual acid content could be reduced by replacing soda-ash with ammonia in the third neutralising bowl. The ammonia treatment produced, however, a slight dulling in the final carbonised product, which could be eliminated by means of a mild bleaching treatment.

Breuers and Blankenburg[104] also studied the efficiency of a variety of neutralising agents. The main parameters investigated were type and concentration of the neutralising agent, temperature, immersion time and liquor-to-fibre ratio. They found that sodium carbonate, ammonia and a combination of ammonia and ammonium acetate were the most effective of all those investigated.

2.5.4 Water Consumption during Neutralising

Mamers[105] carried out a survey on the water usage in a carbonising train and found that 50% of the total water consumption occurred in the first neutralising bowl. He devised an effluent recirculation system which reduced the effluent volume by a factor of four. The plant was operated successfully for over a year with the modified first neutralising bowl, saving several million litres of water to the mill involved in this project.

3. CHANGES IN FIBRE PROPERTIES DURING CARBONISING

Practical experience in the field of carbonising has proved, beyond any doubt, that the various chemical and mechanical stages of this process can cause significant damage to the wool fibre, if extreme care is not exercised at all stages. Damage is associated with changes in the chemical and physical properties of the fibre during the carbonising process itself or during subsequent processing. Assessment of damage and its prevention have, therefore, been the aim of many research workers in this field. Research has been accordingly orientated towards the study of changes in chemical and physical properties and their interrelationship with potential damage and protection of the wool fibre.

3.1 Process-orientated Research

Weclawowicz[106,107] investigated the extent of damage to fibre following (1) carbonising of freshly scoured wool i.e. wet-fibre carbonising and (2) carbonising of dry scoured wool i.e. dry-fibre carbonising and found that the damage was much less in the first case than in the second. Wet-fibre carbonising resulted, on average, in a 5% reduction in tensile strength and no reduction in the value for whiteness, as compared to a 28% reduction in strength and 30% reduction in the value for whiteness for dry-fibre carbonising.

A relatively large number of workers[25,26,28,42,44,51—56,59,65,108—111] investigated the changes in tensile strength, extension at break and alkali solubility of wool resulting from the addition of wetting agents to the acidising liquor and reached similar conclusions on the matter. For instance, Crewther and Pressley[52] reported an increase of 18% in tensile strength, an increase of 34% in extension at break and a decrease of 1,7% in alkali solubility following the addition of wetting agent to the acidising liquor. Mizell and co-workers[56] reported an increase in tensile strength of 17%, while Sadhir and co-workers[44] reported a decrease of 3% in alkali solubility following the addition of a wetting agent to the acidising bowl.

Bendkowska and Zurek[112] investigated the effect of acid concentration in the acid bowl on fibre properties such as alkali solubility and fibre extension at break and reported an increase in alkali solubility from 11 to 20% and a decrease

in fibre extension at break from 22 to 18% with an increase in acid level from 2 to 10%.

The findings of Bendkowska and Zurek[112] were later confirmed to a large extent by Sadhir and co-workers[43,44]. They investigated the effect of an additional parameter, i.e. the immersion time in the acid bowl and concluded that alkali solubility levels obtained by treatment of wools (with a 10 to 15% burr content) with 5,5% sulphuric acid for 10 minutes were too high (above 20%) and that, therefore, a milder treatment for these wools was required[43]. They also found during their studies that a 10% increase in tensile strength of the fibre could be obtained by reducing the acid content from 5,5 to 3,5% (the loss in tensile strength decreasing from 17 to 7%) and recommended that the loss in tensile strength during carbonising be kept as low as possible and preferably below 15% (the corresponding acid treatment level being of the order of 5%).

During another investigation, Latif and co-workers[113] found that the damage caused to the wool fibre during carbonising was not only proportional to the concentration of sulphuric acid and time of immersion in the acid solution, but also inversely proportional to the mean fibre diameter.

In the field of drying and baking, various authors[25,26,65,66,112] agreed that an excessively high moisture or acid content of the wool entering the dryer or an excessively high drying temperature caused an excessive loss in fibre tensile strength. For instance, Mizell and co-workers[25,26] found that an increase in the drying temperature from 65 to 93°C caused an increase in the tensile strength loss from 8 to 19% for an acid content of the wool of 5,7% (corresponding acid content of burrs being 2,5%) and from 15 to 21% for an acid content of the wool of 7,6% (corresponding acid content of burrs being 4,7%). After baking at about 150°C for 3 minutes, however, the corresponding increases in the tensile strength loss were from 8 to 13% and from 20 to 27%, respectively. Burrs were not properly carbonised in the first case (2,5% acid content) but were properly carbonised in the second (4,7% acid content). During the same trials[25,26], the loss in tensile strength was 11% for wool entering the baking unit at a moisture content of 10%, and 19% for a moisture content of 20%. Increasing the baking temperature from about 130 to 150°C (baking time 5 min.) produced a drastic yellowing of the wool but maintained the good handle of the finished product. However, the colour of the wool was satisfactory for a baking time of only 3 min. at 150°C[25,26].

In the field of neutralising, Knott and Zahn[114] investigated the changes occurring during storage in wool carbonised at various acid levels. They found that by merely soaking the wool in water, serious degradation during storage was avoided. An acid content below 1% before storage was required to ensure that carbonised wool would not be damaged. During a further investigation[115], commercially carbonised wool was neutralised to various levels in the laboratory. The samples were stored in a conditioned room for 30 weeks. The

carbonised wool (acid content 3,4%) showed only a slight increase in alkali solubility after soaking in water, whereas the carbonised and neutralised wool (acid content 0,6%, pH 4) showed no increase in alkali solubility whatsoever after a similar treatment.

Bauer[73] investigated the occurrence of soluble wool-substance caused by the carbonising process. He carried out tests on commercial samples from the feed and delivery lattices of a neutralising bowl and found a substantial fibre loss of 2,4% on average. The percentage mass loss of fibre in neutralising increased from 2,5 to 3,4% with an increase in the concentration of sulphuric acid during acidising from 3 to 5% and from 3,4 to 5% with an increase in baking temperature from 115 to 135°C. Bauer[73] suggested that acid hydrolysis of the wool protein might have been one of the factors resulting in fibre loss and subsequent nitrogen analyses supported this theory.

The mass loss of fibre during carbonising as a whole has been the topic of concerted studies during the late 1970's [116—118]. It was reported[116] that, under normal carbonising conditions, there was only a very small loss of wool during the acid treatment, but that more significant losses took place during the subsequent neutralising stage, varying in accordance to the neutralising conditions. For instance, studies on neutralising of carbonised wool with water, dilute ammonia and dilute sodium carbonate[116] showed that wool dissolved to the extent of 0,1%, 0,5% and 1,7% in these three cases, respectively.

The Australian Wool Corporation undertook large-scale studies[117,118] on behalf of eight carbonising mills to establish a formula which could be used by laboratories to convert core-test results on greasy wool[119] into an estimated commercial carbonising yield. The studies involved 90 commercial batches of merino and crossbred wools, ranging from 41 to 434 bales per batch, with a wool base range from 35 to 55% and vegetable matter from 2,9 to 18,5%. It was found that the wool base was directly proportional to the actual commercial carbonising yield. The average carbonising loss was found to be 3,05% on an oven-dry basis (about 3,6% at 17% regain). This average carbonising loss of about 3,6% seems highly significant when considering that it meant a worldwide loss of nearly 1420 tonnes of wool[16] during 1984.

A number of authors [120,121] investigated changes in certain properties of carbonised wool. Cegarra[120] discussed the merits of the alkali-solubility test as a method for determining the degree of fibre modification during carbonising and the influence of certain factors (such as country of origin of the wool) on the alkali solubility of carbonised wool. He reported that South African wools had, on average, an alkali solubility of 15,6%, Argentinian wools 16,8% and Australian wools 17,3%.

Garrow and co-workers[121] showed that the whiteness of certain types of carbonised wools could be improved by exposure to blue light. The cost of

operating a conveyor-type system using commercially available sources of blue light was assessed and found to be only marginally lower than the monetary benefit accrued from the increased price of wool.

3.2 FUNDAMENTAL RESEARCH

A large number of authors[64,99,113–116,122–146] carried out basic research into various factors affecting carbonising of wool and found that a series of reversible and irreversible chemical changes took place during the process. Zahn[122], for instance, found that the total sulphate content of wool increased by 370%, the number of amino groups by 57%, the urea-bisulphite solubility by 17%, the alkali-solubility by 12% and the tryptophan content decreased by 16% during the carbonising process. On basis of these findings, it was recommended[122] that the total sulphate determination be used for assessment of damage in wool from the baking oven and alkali solubility for routine testing of wool after neutralising. Zahn[123] also found that (1) carbonised wool contained about double the number of serine and threonine amino end-groups (amino acids which contain hydroxyl groups), whereas the other end-groups were not affected, (2) dry storage led to a further increase in the number of serine and threonine end-groups and had some effect on the glycine and valine end-groups, (3) humid storage resulted in a much faster increase in end-groups and (4) neutralised wool contained fewer serine and threonine end-groups, whereas the end-groups of the other amino acids remained unchanged or increased slightly.

These findings can be best explained[123] by assuming a partly reversible $N \rightarrow O$-peptidyl shift (as shown in Fig. 1) in the serine and threonine amino residues during carbonising. This shift can be reversed when neutralising of carbonised wool is carried out immediately after baking[123]. However, only a very small proportion of the serine and threonine peptide links are involved in this shift. Carbonising increased the number of free serine amino groups from 0,27 to 0,77%, expressed as a percentage of the total serine content, and of free threonine from 0,84 to 1,16%. The reversibility of this process during neutralising (see Fig. 1) was found to be at the most 60%.

Hille and Zahn[99] further investigated the $N \rightarrow O$-peptidyl shift occurring during carbonising and found that the process caused a specific increase in the number of serine and threonine amino end-groups. Since the number of end-groups decreased towards the original value during the $O \rightarrow N$-peptidyl shift occurring during neutralising, the authors recommended that carbonised wool be, in fact, completely neutralised by pH adjustment to a slightly alkaline level of 8,6. The final product obtained at this pH value compared favourably with partially neutralised wool from the point of view of chemical properties. The authors also reported that complete neutralising to a pH level of 8,6 produced a recovery of serine peptide bonds of 80% and, in the case of threonine, of about 70%[99].
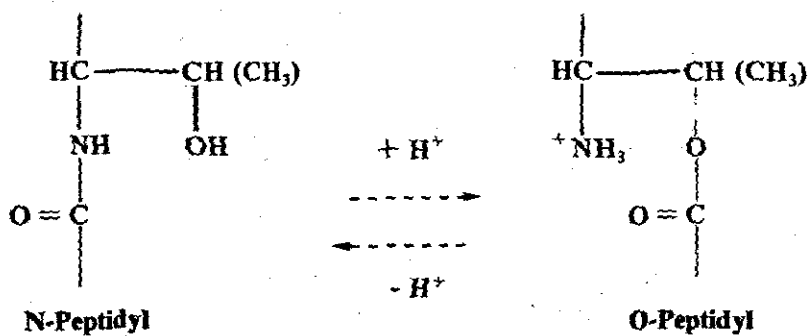
Fig. 1 – *Illustration of the N→O-peptidyl and O→N-peptidyl shifts occurring during carbonising*[123].

A number of authors [64,114,115,124,125,129,131—138] attempted to identify and explain a variety of chemical reactions occurring during carbonising. Knott and Zahn [114,115,124,125] studied the chemical modifications of wool during (1) acidising, (2) drying and baking and (3) neutralising, under industrial conditions. They found no variation in the composition of the amino acids after the various stages of carbonising but detected some N→O-peptidyl shift during acidising and a marked shift during drying and baking[124]. Furthermore, they confirmed[127] their previous findings relating to the O→N-peptidyl migration occurring during neutralising[99] and found that neutralising inhibited further N→O-peptidyl shift during storage[115]. Knott[125] observed a distinct tendency for alkali solubility to increase with an increase in N-terminal amino acids, particularly serine and threonine.

Asquith[131] investigated the formation of transversal bonds during carbonising of wool and found that during acidising, sulphur was bound to the fibre in three different manners, i.e. (1) as hydrolysable sulphur, which could be recovered as sulphuric acid by hydrolysis of the fibre, (2) as sulphur bound to the fibre by covalent bonds, which can be recovered by hydrolysis as stable derivatives of amino acids and (3) as sulphur in the form of sulphate, which was bound by ionic bonds to the fibre and which could be recovered by either pyridine or sodium carbonate extraction before the hydrolysis was carried out.

Several workers[129,139—141] investigated the causes of unlevel dye affinity of carbonised wools. Malek and co-workers[129] found that the serine and threonine end-groups reacted with sulphuric acid and this had an adverse effect on the dyeing of carbonised wool. Blankenburg and co-workers[139] found a definite correlation between the covalent sulphate content of carbonised wool (which

reached levels as high as 2,7% in damaged lots) and the quantity of fixed dye. Blankenburg and co-workers[139] also found that other factors such as residual grease content of the wool and the effect of weathering were parameters which modified the dye affinity of wool. Sensitive dyeing tests were developed [140,141] to assess damage and, hence, potential uneven dyeing of carbonised wool.

Several workers[113,126—128] investigated the apparent increase in cysteic acid content of wool during carbonising. La France and co-workers[126] found that the values obtained by low-voltage paper electrophoresis were erroneous as a result of the presence and interference of two other components, i.e. o-serine acid sulphate and o-threonine acid sulphate. Bielen[127] found that the cysteic acid contents of well-neutralised carbonised wool and scoured wool were approximately the same. Furthermore, Latif and co-workers[113] found no differences in the cystine and nitrogen contents of untreated and carbonised wools while Satlow and co-workers[128] found no marked changes in the cysteic acid and tryptophane contents of untreated and commercially carbonised wools.

A number of workers [126,131,132,134—138] carried out fundamental research related to a specific area of carbonising i.e. (1) acidising, (2) drying and baking and (3) neutralising. For instance, Malek and co-workers[129] found that sulphuric acid attacked the fibre according to two reactions mainly i.e. (1) hydrolysis of the peptidyl links and (2) chemical reaction of the acid with amino acids of the wool. Other types of reactions involved sulphuric acid attack on the benzene ring of other wool compounds and resulted in the formation of sulphonic derivatives.

Asquith[131] found that, following severe acid treatment of wool (for 10 minutes), its total sulphur content increased from 3,9 to 7,4%, while its cystine content decreased from 11,4 to 10,5%. Asquith[131] carbonised these wool samples at 122°C in the laboratory and found that the total sulphate content of these samples increased by 2% in absolute value (from 1,9 to 3,9%) when the sulphuric acid concentration during acidising was 5% and by 3,1% (from 2,8 to 5,9%) when the acid concentration was 10%.

Hepworth and co-workers[142] studied the surface topography of carbonised un-neutralised wools by means of a scanning electron microscope and found that wool fibres which had been acidised with sulphuric acid in the presence of a detergent were smoothed and the distal edges of their cuticular cells were slightly lifted while some of their clefts were widened. The same changes were observed to a greater degree when the detergent was absent and actual degradation was also seen to have occurred. The authors concluded that, in the absence of a surfactant, sulphuric acid produced greater damage in localised areas, and this led to the conclusion that surfactants promoted a more even spreading of the acid on the fibre. Hepworth and co-workers[142] also found that when these carbonised wools were neutralised with soda ash, they appeared to have had undergone a very mild attack which caused only slight lifting of the

cuticular-cell edges and widening of the clefts.

Asquith[132] found that a number of reactions occurred during the drying and baking stages of carbonising. During drying, the acid was effectively concentrated from 5% to about 80% as the water evaporated. At the drying temperature, these acidic conditions could easily result in hydrolysis of the peptide bonds. Another study[133] concerned with the rate of hydrolysis of wool in sulphuric acid clearly showed that even at lower temperature rapid hydrolysis and dissolution occurred when the acid concentration ranged from 40 to 70%. This degradation could not be ascribed entirely to peptide bond hydrolysis, as studies on the amide nitrogen content of acid-treated wools had indicated that hydrolysis of side-chain groups was faster at acid concentrations around 45%. Presumably, for higher acid concentrations (between 45 and 70%) the rate of fibre dissolution would increase[132].

Chemical reactions during baking appear to be of a complex nature[64,126,132,134—138]. One study[132] revealed that wool treated in the cold with concentrated sulphuric acid (80 to 96%) became resistant to dyeing with acid dyes. Further studies[135—137] could not conclusively pinpoint the exact sequence of reactions occurring during baking. However, strong evidence was presented to suggest that the sole sulphation reaction was the esterification of hydroxyl groups. Careful acid hydrolysis of carbonised wool had previously been reported[126] to result in small traces of serine-o-sulphate ester being detected in the hydrolysate and studies on enzymatic hydrolysates of carbonised wool[138] enabled serine-o-sulphate to be identified and obtained in significant quantities. It was suggested[138] that dyeing faults could be attributed to the presence of an excessive number of serine-o-sulphate groups.

Zahn[123] found that the value for alkali solubility of freshly carbonised wool varied in accordance to its sulphuric acid content, that carbonised wool which was not neutralised and was stored under high-humidity conditions showed a progressive increase in alkali solubility and that under similar treatment conditions, dry storage did not affect the alkali solubility significantly.

Malek and co-workers[129] established that, as a result of sulphuric acid attack on the fibre, there was a loss of mass of fibre brought about by dissolution of protein matter in the neutralising bowls. The extent of this loss was variable and dependent on many factors such as acid concentration, moisture content of the fibre and presence or absence of protecting agents. Another study[116] established that fibre dissolution in the neutralising bowl was mainly in the form of tyrosine-rich proteins. It was also believed that some of these proteins were located in the cuticle and cell-membrane complexes and that their removal was expected to affect dyeing performance.

3.3 MONITORING OF A CARBONISING LINE

All five stages of carbonising i.e. (1) scouring, (2) acidising, (3) drying and

baking, (4) burr-crushing and dedusting and (5) neutralising require careful monitoring with a view to producing a good quality carbonised product, containing as little as possible residual vegetable-matter and acid. The aim of this section is to provide the reader with information about chemical and physical testing procedures of particular interest in the monitoring of the carbonising process.

3.3.1 Scouring

It is customary to have core test certificates on each carbonising lot before it enters the scouring stage of the carbonising plant. These documents provide test results of wool base[119], vegetable matter base[119], clean wool content[119], scoured yield[119] and mean fibre diameter[147]. In order to assess the change in properties and possible damage to the fibre during carbonising, it is useful to also determine at this stage fibre length[148], fibre strength[149—151] and alkali solubility[152] (or alternatively, urea-bisulphite solubility[153]). The grease content of the greasy wool can be determined[154,155] prior to scouring and the residual grease content of the wool leaving the rinsing bowl and entering the acidising bowl should be monitored on a routine basis[154] (this allows for detergent additions during scouring to be established).

3.3.2 Acidising

Already in the 1940's and early 1950's, von Bergen[156,157] suggested that the acid level in the acidising bowl should be continuously controlled by titration of aliquots and not by specific gravity measurements, which were affected by accumulation of sodium sulphate. This was confirmed later by Bielen[158], who found that titrimetric measurements[159] were ideal when monitoring the acid content on a routine basis.

Some work was also carried out on methods for determining the concentration of surfactant in the acid bath. Nossar and Edenborough[160] established that the time for a metallic device to sink in a particular acid liquor was a function of surfactant concentration and this could be used as a measure of the surfactant concentration of that liquor. The authors claimed that, for practical purposes, the mean of ten measurements of the so-called "sinking time" gave a reliable and rapid estimate of the surfactant concentration.

The acidified and squeezed wool emerging from the squeeze rollers of the acidising bowl should be carefully monitored for acid content[161] and moisture content[162,163]. This monitoring is necessary in order to avoid damage to the fibre during the subsequent stages of carbonising.

3.3.3 Drying and Baking

During these two phases of carbonising the residual moisture contents of

wool are of paramount importance and should be carefully monitored on a routine basis[162, 163]. Also, temperatures should be maintained below certain critical values during both drying and baking (see section 2.3).

3.3.4 Burr Crushing and Dedusting

Haly and Hafey[23] developed a mechanical test for burr brittleness. A loosely-packed burr sample was placed in a specially designed test cell, equipped with a plunger. The whole assembly was placed on a compression cell in an Instron Tester, and the force exerted as the plunger was driven down at constant rate was recorded. The maximum value for the force was taken as the brittleness index.

During carbonising, both the burr-crusher and deduster units have to be carefully monitored for fibre losses. Should this occur to a significant extent in any of these units, it would mean that the unit in question needed re-setting. The rollers of the burr-crusher should not be set too tight to avoid damage to the fibre, but tightly enough to enable efficient crushing of the burrs. The combs of the deduster should be set to avoid fibre breakage while ensuring efficient burr removal.

3.3.5 Neutralising

Both the pH of the aqueous extract of the wool[164] and the pyridine method for residual acid[161] have been reported to give a measure of the state of neutralising of the wool. However, it is considered a rather complex task to obtain neutralised wool at a desired pH value[98], since the pH of the neutralising bowl does not necessarily determine the final pH of the wool[165]. Such sensitive control of the neutralising process is believed to be only possible[98] by careful adjustment of the level of soda-ash in the neutralising bowl.

3.3.6 Quality Control of Carbonised Wool

The carbonised and neutralised wool should be normally tested for residual vegetable-matter content[119], in order to assess the efficiency of the process. Following this, the quality of the wool should be controlled at this stage by testing fibre length[148], fibre strength[149—151], alkali solubility[152] (or, alternatively, urea-bisulphite solubility[153]) and whiteness[166—169] and relating the results from these tests to those obtained previously for the same wool lot before carbonising.

Over the years, standard values for the chemical properties of carbonised wool have been published. Historically, these values were first established during the late 1960's and the relevant information, which has been reported by Zahn, Knott and Blankenburg[170—173], is given in Table 1.

A number of additional testing procedures have been developed to assess

the damage to wool during carbonising. During the late 1960's, IWTO published[174] a testing procedure to determine the feltability of wool (Aachen Felting Test). Also during the late 1960's, Juneja and co-workers[175] attempted to estimate the brittleness of wool fibres as a measure of damage due to carbonising. Juneja and co-workers showed that measurements of the breaking twist angle of wet fibres constituted a more accurate and reliable test compared to other measurements commonly used for detecting carbonising damage in wool. The authors stressed that knowledge of the brittleness of wool could be useful in ascertaining its processing performance during operations which follow the carbonising process.

TABLE 1
STANDARD VALUES FOR CARBONISED WOOL

Chemical Property	36th International Conference in Brussels (1967)	Kulenkampff Working Group (1969)
pH of Aqueous Extract	4-8	4-7,5
Acid Content (%)	max. 1,0	max. 0,9
Alkali Solubility (%)	11-25	11-22
Dichloromethane Extractable Matter (%)	—	max. 1,0

During the early 1970's, Edenborough and Nossar[176] developed a tensile strength test using non-combed flat fibre bundles and an Instron Tester. The testing method was reported to give a more accurate estimate of fibre damage during carbonising than that obtained on the basis of conventional tenacity measurements.

During the late 1970's, Knott and co-workers[140] reported that the determination of α-amino groups by the ninhydrin method was a sensitive test which can be used to detect degradation of wool during carbonising. The ninhydrin method was reported to be faster and easier to perform than the alternative dinitro-phenylation (DNP) method for determination of α-amino groups and this made it more suitable for industrial laboratories[140].

4. MODIFICATIONS TO THE CONVENTIONAL CARBONISING PROCESS

4.1 USE OF SUCTION-DRUM TECHNOLOGY IN CARBONISING

During the period 1965 to 1972 a number of patents were taken out by Fleissner on a modified sulphuric acid carbonising process[177–179]. These modifications involved the use of suction-drum technology at the various stages of the process. Acidising was reported[179] to be carried out by means of a rotating sieve drum subjected to a suction draft, with the acid solution being forced through the wool from the outside to the inside of the drum. The process also invoved a suction-drum conveying unit to remove liquid from the acidised wool, an extraction unit to further remove water and acid from the wool, a drying and baking unit using suction-drum technology, a mechanical unit to remove carbonised material from the wool and a suction-drum-based neutralising unit[179].

Motlova[180] carried out an investigation into the performance of a suction-drum-based continuous carbonising plant, operating in Czechoslovakia. The plant consisted of (1) a two-drum wetting bowl, (2) a three-drum acidising bowl, (3) a six-drum dryer, (4) a two-drum baking unit, (5) two complete sets of twelve-roller crusher and beater units, (6) a one-drum rinsing bowl, (7) a three-drum neutralising bowl, (8) two one-drum rinsing bowls and (9) a four-drum dryer. Motlova found that carbonising performance was improved when a cooling source was connected to the acidising bowl to keep the acid solution at a low temperature[180]. Motlova also found that an acid immersion time of between 1,5 and 2 mins (depending on the type and amount of burrs) was the most suitable for acid concentrations in the bowl ranging from 5 to 7,5%.

Drying time were optimum in the range of 2 to 4 mins and the most suitable drying temperature was 80°C. Recommended baking conditions were 120 to 130°C for 2 to 4 mins. The neutralising bowls were best operated on a counter-current principle and alkali added only into the three-drum neutralising bowl. Performance trials also showed that the removal of vegetable matter was excellent and production rates surpassed those previously obtained[180].

In recent years, Fleisner[181], have re-designed their carbonising line. The new carbonising plants are provided with an acid treatment section with feeder, conveyor, weighing scale and opener, followed by a wetting bowl and an acid bowl. The bowls in the wool scouring section as well as those in the neutralising section operate with perforated drums, which are reported[181] to ensure good acid impregnation and penetration of the wool. A steel hopper and a squeezer with oscillating conveyor are mounted in front of the dryer and baking units to obtain a more uniform wool input. The wool is dried at a relatively low temperature (60°C) in a perforated-drum dryer and then subjected to a short baking period at 120 to 130°C. The baking zone is separated from the drying zone and linked to it

by a ventilated conveyor. This conveyor also runs beneath all the perforated drums of the drying zone, collecting and transporting fibres and vegetable matter to the outlet of the baking unit. The assemblies of the subsequent step-cleaner and crusher units have been re-designed, the latter unit having been provided with a pneumatically-operated and infinitely-variable roller pressure adjustment. Neutralising and rinsing takes place in several perforated-drum scouring bowls and final drying is done at a temperature of 80° C. Other features of this plant include a central control station, dosing equipment for acid and alkali and regulating sytems for temperature and exhaust air[181].

4.2 THE RAPID CARBONISING PROCESS

During the mid-1960's, Moncrieff[182,183] reported that burry wools could be satisfactorily carbonised by treatment with a 7% solution of sulphuric acid (at room temperature) containing 0,15% of a nonionic surfactant. The novel feature of his studies was the use of a higher acid concentration than usual and a relatively short immersion time of between 0,5 and 5 mins. Moncrieff[182,183] found that, while burrs absorbed the maximum amount of acid very quickly, i.e. within half a minute to one minute depending on the nature of the burr, wool took longer to reach the maximum level of acid absorption (of the order of 3 mins). It became clear in later years[39], particularly after the advent of the "Rapid Carbonising Process", that even shorter immersion times can give satisfactory results.

The "Rapid Carbonising Process" was developed by Nossar, Chaikin and co-workers[28,58,95,184—191] at the University of New South Wales. This novel process for carbonising was claimed [17,184] to minimise wool fibre entanglement and damage while opening new possibilities in the field of worsted yarn manufacture, particularly as far as the use of burry wools for the production of tops was concerned. The development of this process started with trials on a pilot acidising plant[58,185]. The successful outcome of these trials led to the design of an industrial prototype, which consisted basically of two conveyor belts which held the wool while it was being treated with acid liquor. The wool was fed through three pairs of squeeze rollers exerting a moderate pressure. This arrangement ensured proper wetting-out of the burrs with a 7 to 8% acid liquor, supplied via three flooded spillways, within the relatively short time of between 45 and 60 seconds[28,184] (representing the total time for acidising and squeezing). Addition of nonionic surfactants of the nonylphenol polyethylene-oxide type (particularly those of a short chain length) to the acid liquor proved to be more effective in reducing carbonising damage to the fibre than that of an anionic type, such as sodium dodecyl benzene sulphonate[189].

Research on rapid drying and baking was carried out on a pilot plant[186], similar in design to an industrial prototype built by Petrie and McNaught in the United Kingdom. It was found that the time which elapsed between the acid

treatment and drying played an important role in the process[186] and that during the drying and baking stages it was important that wool fibres were dried quickly and uniformly to prevent acid damage[187]. The design of an industrial prototype machine allowed for rapid drying and baking (in less than 40 seconds) at relatively high temperatures e.g. $150°$ C[28,184]. Longer baking times, i.e. of the order of 3 mins were obtained by using additional baking sections.

Experiments with a pilot burr-crusher revealed[28,184] that damage to fibres occurred only when these became trapped between the burrs and the fluted rollers of the machine. To solve this problem, the "Rapid" industrial prototype included a hopper feeder, which allowed for a thin layer of wool to be supplied to the eight pairs of crushing rollers (these rollers had each a different geometry but were all running at the same surface speed). A progressively closer setting between the first five pairs of rollers ensured that larger burrs were crushed first, without imposing large forces on the attached fibres. Trials with this industrial prototype indicated that an improvement of at least 3 mm in the mean fibre length of the finished tops could be expected by processing wool with this crusher compared to a conventional one [28,184].

Since conventional neutralising of carbonised wool with soda-ash required a treatment time of the order of 3 mins, Nossar and Chaikin[28, 184] modified the neutralising bowl to suit their rapid process. Smaller rapid-neutralising units were designed and pilot plant work[28,184] showed that it was possible to neutralise wools down to about 0,1% residual acid content by means of a 40-second immersion in an 0,1% ammonia solution (which does not produce an objectionable odour). Later studies[188] confirmed that rapid neutralising of wool using weak and practically odourless ammonia solutions (0,2%) was possible, particularly when the wetting-out of the wool was improved by the addition of a surfactant to the neutralising bowls. It was also possible to reduce the immersion time to only 30 seconds[95]. The authors concluded[188] that a flat-bed neutraliser using a 0,2% ammonia solution and a surfactant was likely to be a practical proposition for industry.

Bell[192] and Edenborough and co-workers[190] discussed critically the economic advantages and disadvantages of rapid carbonising. Furthermore, extensive industrial evaluation trials[191] were carried out in Australia for a period of one and a half years, using the Rapid Carbonising Process. The results of these trials showed that the carbonised product obtained by means of this process was superior in strength, openness and colour to conventionally carbonised wool. Also, the new plant occupied considerably less floor space than the conventional one and was capable of substantially higher production rates[191]. In spite of these findings, however, no evidence of commercial application of this process has been found in the literature.

4.3 MISCELLANEOUS

Oku and Shimizu[193] found that chemical pretreatment of greasy wool (prior to carbonising) with an acidic solution of hexamethylenetetramine in the presence of a nonionic surfactant resulted in the wool becoming alkali-resistant and almost totally degreased. Oku and Shimizu also found that damage during subsequent carbonising was considerably reduced when this chemical pretreatment was carried out at relatively low temperatures (35°C). No evidence has been found in the literature of any industrial application of this novel idea, perhaps due to the additional costs incurred by this pretreatment.

Hopfer[194], von Hornuff[195], Frieser[196] and Haly and Hafey[23] reported on the use of aluminium chloride and hydrochloric acid instead of sulphuric acid for acidising of wool. According to Frieser[196], the advantage of this technique lay in the gentle fibre treatment it provided. However, it was obviously a more costly process than the more conventional sulphuric acid process. Also, baking temperatures required for this process (120°C to 130°C) were considerably higher than those used for the sulphuric acid process in those years, so that it was suspected that this could lead to wool damage. However, in the currently used sulphuric-acid process, baking is carried out in that very same temperature range and damage to wool, if and whenever it occurs, is normally attributed to the drying and not the baking stage[39]. The acid mixture used for this purpose consisted of 2 to 3 parts of aluminium chloride for every part of hydrochloric acid, to yield a density of 6 to 10° Bé[196]. Acidising was reported to be the critical stage which affected wool quality, while the drying stage played only a minor role. Carbonising was reported to be more uniform with these chemicals than with sulphuric acid and the aluminium hydroxide produced by hydrolysis was found to be completely removable from the wool by chemical means. However, it was reported[196] that a 0,2% aluminium hydroxide residue remained on the fibre.

More recently, Haly and Hafey[23] carried out some laboratory studies involving the use of aluminium chloride and hydrochloric acid for carbonising. They concluded from their studies that (1) hydrochloric acid had some difficulties in diffusing into the burr and that (2) levels of aluminium chloride as high as 10% (on the mass of wool) were required to carbonise the burrs properly. They also found[23] that treatment with hydrochloric acid gas was equally discouraging, since the burrs seemed partially protected from acid attack while the fibre was prone to damage by local high concentrations of hydrochloric acid.

5. CONCLUDING REMARKS

Modern technological developments in the field of raw wool carbonising have been reviewed, alongside the more conventional techniques. A fairly large amount of research work has been carried out in this field and it has emerged

that the sulphuric acid process is by far the most viable at present. Furthermore, it has emerged from this review that undue damage to wool fibre can be avoided by careful monitoring of the carbonising process. Parameters to be monitored are (1) acid content, surfactant concentration, temperature and residence time in the acid bowl, (2) moisture content of the wool entering the dryer and temperature and residence time in dryer, (3) residence time in the baking oven and baking temperature, (4) settings of the burr-crushing rollers, (5) setting and speed of the dedusting unit, (6) neutralising sequence opted for (i.e. combination of soda-ash, mild scouring and rinsing bowls which is adopted) as well as soda-ash concentration and residence time of wool in the neutralising bowls and, finally, (7) residual acid content, pH of the aqueous extract, alkali solubility, colour, tensile strength and extention at break of the carbonised product. The efficiency of the carbonising process can be effectively monitored by measuring the residual VM content of the carbonised product.

In spite of the vast amount of knowledge available on the carbonising process, there is some lack of information in certain confined areas. For instance, information about the best conditions for acidising, drying and baking for the removal of the main vegetable matter types is very largely confined to in-house knowledge gained by industry itself and which is not available elsewhere. The same may be said about the effect of various scouring conditions on the actual carbonising process and the effect of various carbonising conditions on different types of wool, as well as their individual effect on subsequent processes in both the worsted and woollen systems. Apart from the need to gain knowledge in these fields, there is a great need for research in the area of fibre loss caused by the carbonising process.

USE OF PROPRIETARY NAMES

The names of proprietary products where they appear in this report are metioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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