

Andrzej Kucharski,
Józef Świątek*,
Zbigniew Wrocławski*

Factory of Special Production 'Pionki'
26-670 Pionki, Poland

*Polmatex-Cenaro Research
and Development Centre of Textile Machinery
ul. Wólczańska 55/59, 90-608 Łódź, Poland
E-mail: biuro@cenaro.lodz.pl

Intensification of Mass Exchange in Physico-Chemical Processing of Fibrous Materials in a Liquid Medium

Abstract

Physico-chemical processing is very often used in the textile and paper industries, and in the industry of high-energy materials based on nitrocellulose. Mass exchange in these processes depends on the specific features of the form and structure of the parent substance (reactant). Notwithstanding the differences among the reagents used in the above-mentioned industries, the mass exchanging processes are similar. As liquids acting therein, we have dyes and bleaching agents used as solutions in chemical processing of fibres, acids and inorganic alkali in paper manufacturing, and nitric acid with compounds which form hydrates in the nitration process of cellulose. In general, in all these processes the motion of mass takes place together with chemical reactions of an additive or exchange character. The problems of mass exchange are analysed in this article from the point of view of the designers and constructors of machines and apparatuses which must perform the processes mentioned above. This analysis is based on the characteristic criteria of similarity between quantities, considering the geometric, energetic, and dynamic conditions which determine the process intensity. It has been proved that, according to the present state of knowledge and technique, the laminar liquid wall-surface layer which surrounds the fibrous parent substance acts as the main resistance for mass motion. It is possible to decrease this layer by several times (even over 30 times), and by this means significantly intensify the process. A process intensification criterion is presented.

Key words: mass-exchange, fibrous materials, cellulose, nitrocellulose, nitration, process intensification, scale changes.

Introduction

The world resources of crude oil which are known of at this point in time will run out in about 25 years according to present forecasts, and within the period of one generation mankind will confront the necessity of finding sources of renewable industrial raw materials for different applications. One such basic renewable raw material is cellulose, which consists of the basic fibrous component of plant structure. Improvement in the chemical processing of this parent substance is an urgent need at present.

The chemical processing of fibrous materials is a common operation in the textile and paper industries, as in the industry of high-energy materials based on nitrocellulose. The mass exchange in chemical processes characteristic for these industries, which led to the transformation of the materials mentioned above, depends on the peculiar initial features of the parent substance's form and structure which distinguish them from other parent substances commonly used in chemical production. The following features can be listed as the most crucial:

- small thickness of the fibre within the range of $d = 1-15 \mu\text{m}$,
- fibre length many times greater than the thickness ($l \gg d$),

- relatively small parent-substance density (ρ_f) which differs only slightly from the density (ρ_l) of most liquids used in the processes under consideration ($\rho_f \approx \rho_l$),
- considerable cohesion of the fibres,
- a tendency of the fibrous suspension to cluster in liquids, and
- in many cases, a tendency of the conglomerations formed to felt or to form solid mechanical consolidations.

Although the particular reagents differ in the various chemical reactions of fibrous materials' processing, the processes itself are similar, if the character of mass motion is considered. Dyes and bleaching agents used as aqueous solutions (or solutions with other solvents) act as reagents in the chemical processing of textiles; acids and inorganic alkalis act in paper manufacturing, and nitric acid with compounds which form hydrates (most often sulphuric acid) act in the nitration process of cellulose. In the latter case, the hydrates bind the water which is formed in the estrification reaction. In all the processes considered, the motion of mass takes place together with an additive or exchange chemical reaction which accelerates or retards the motion of mass. In the case of dyeing, the reaction is mostly additive which may accelerate the mass motion, whereas in the instance of nitration, the exchange takes place in two

directions: the nitric acid diffuses into the fibre inside, whereas water (which is created in the fibre as the result of cellulose estrification) diffuses to the medium surrounding the fibre. This process has an exothermic character, as well as a contemporaneous chemical reaction which takes place retarding the mass motion, together with a contemporaneous heat exchange in the direction opposite to the acid motion. These examples of mass motion indicate the complex character of the problem considered, and in connection with this, the difficulty and complexity of describing the process within the framework of a generalised theoretical elaboration.

The form of the parent substance has a fundamental influence on the flow phenomena which accompany the mass motion and chemical reaction. The parent substance's form and structure determine the generally accepted designs of apparatuses and installations in the textile and cellulose & paper-making industries, but it unfortunately has not been used as the guiding feature in the construction of apparatuses for nitrocellulose manufacturing. It should be emphasised here that the equipment and apparatuses for mass exchange in the textile and paper industries (and partly also those for cellulose nitration) differ from those generally known in chemical engineering. These

latter apparatuses, destined for different processes, have been the subjects of many good theoretical elaborations.

An enormous development within the branch of chemical processing of fibres was observed in the textile industry after 1945, whereas the new constructions for cellulose nitration did not extend beyond stereotypical solutions. However, this progress has not been based on the theoretical elaboration of the question of mass exchange, but had its origin in the splendid intuition of experimenters in science and industry which led them effectively to the appropriate goal. These processes have been considerably intensified, the costs decreased, and in consequence the quality of products has risen. Considerably less progress has been observed in the development of apparatuses for cellulose nitration. A discerning analysis of this industry allows us to state that the reason for such a situation results in the presently existing surplus of the total world production efficiency, and the relatively peaceful time periods on Earth which do not essentially force a need to improve the gun-powder manufacturing process.

■ Process Analysis

The problem of mass exchange has been analysed in this article from the point of view of the designers and constructors of machines which must perform this process, and takes into consideration all the conditions which the constructor is able to secure for a good proceeding of the process. These conditions are of the following nature:

- geometrical (formation of elements performing the process),
- energetical (supply of mechanical energy, supply or carry away heat), and
- dynamic (mechanical functions and activities connected with forcing the motion of reagents).

The most substantial questions connected with these conditions are: mass exchange, the surface of mass exchange, the form of the fibrous material agglomerations, forced liquid motion & the liquid wall-surface-layer, and layer porosity; all of these are discussed in the following subchapters (a-e):

a) Mass exchange

Mass exchange proceeds by diffusion, convection, and by diffusion and convection together. Diffusion takes place

in every existing phase (gaseous, liquid and solid) and from any of these phases to the other. Diffusion proceeds slowly (in comparison with other ways of mass exchange); what is more, it occurs only rarely in industrial processes in pure form, as it is difficult to maintain complete immobility of gases or liquids. The mixing of agents appears in all processes in one way or another, which means that the displacement of agents from an area of higher concentration to those of lower concentration takes place in a mechanical way. Pure diffusion exists only in solid bodies and in the liquid wall-surface layer surrounding the solid parent substance.

In general, mass exchange can be considered by analogy with heat exchange. The action of both processes is similar. Mass motion by diffusion (which can be designated as 'mass conduction') is governed by analogical laws such as heat conduction. The well-known Fourier equation is constructed on the assumption that the heat amount Q conducted through a given surface F , over an infinitely small time period $d\tau$, is proportional to the relative temperature gradient dt/ds (in the normal direction to this surface) and to the value of this surface (F):

mass

$$dQ/d\tau = \lambda \cdot F \cdot dt/ds \quad (1)$$

where the proportionality coefficient λ (which here is heat conductivity) depends on the properties of the conducting agent.

Fick's law which describes diffusion (the conduction of the agent within a particular phase) is constructed analogically. The amount of agent over an infinitely small time period ($dV/d\tau$) is proportional to the conducting surface and to the concentration gradient (dC/ds):

$$dV/d\tau = -D \cdot F \cdot dC/ds \quad (2)$$

where D is the diffusion coefficient.

The identity of the structure of both these equations is visible. The equations considered can be simplified and easily integrated in the instance of heat, as well as of mass conduction stabilised over time, and Fick's equation can be presented (after integration) in weight units:

$$G = -\delta \cdot F \cdot (C_2 - C_1)/s \quad (3)$$

where:

$\delta = D/\rho$, and
 ρ - density.

Mass exchange between phases is described in weight units by equation (4):

$$G = \alpha_m \cdot F \cdot (C_2 - C_1) \quad (4)$$

where:

G - is mass in weight units, and
 α_m - is the coefficient of mass permeation between both phases.

The exchange resistances of mass motion can be summarised similarly to those of heat motion. Finally, the interesting (for the designer of the apparatus) resistance can be presented by an equation analogous to that corresponding to heat exchange:

$$G = k_m \cdot F \cdot (C_2 - C_1) \quad (5)$$

with the coefficient interrelation:

$$1/k_m = 1/\alpha_m + s/\sigma \quad (5a)$$

where: k_m is the mass permeation coefficient.

However, the problem becomes considerably more complex in the case of mass exchange, and in reality it does not look so simple. In heat motion only one kind of energy is transmitted, whereas in mass exchange we usually work with some various kinds of mass, most often with chemical compounds, moreover often dissolved and diluted compounds. As an example, dye mixtures act in fibre dyeing, and nitrous acid (a compound which creates hydrates (in general sulphuric acid)) acts in cellulose nitration together with water. The dependence of the diffusion coefficient on the temperature is significantly non-linear, and the phenomenon of mass exchange depends on the concomitant chemical reactions, the number, and the mutual interactions of various components; all these conditions complicate the problem significantly. After all, the results obtained by a given experiment, as also by a natural experiment¹ can be compared under similar conditions and used as model data, especially when changing the scale of the process or the apparatuses, and when designing a new generation of technological processes and installations on the basis of exploitation experience obtained from the process and installation of a previous generation.

b) Surface of mass exchange

The problems connected with determining the mass exchange surface of a fibrous substance are just as complex as those with the total coefficient of mass exchange. Fibrous structures, especially

those of plant origin such as cotton, bast fibres, and wood cellulose, whose framework consists of cellulose with molecular chains of various length arranged parallel into some domains and consolidated by intermolecular forces (which ensure an anisotropy structure), have a micellar structure, and their inner surface is very spread out, within the range of $(2-4.5) \times 10^6 \text{ cm}^2/\text{cm}^3$. Mass motion inside natural fibres is a diffusion process which can be considered as performed in a homogeneous body without taking into consideration the fibre's structure which is similar to that of synthetic fibres. In the case of the fibrous form of a solid body, the fibre length l is many times greater than its diameter d ($l \gg d$). From this it results that the fibre surface F as a function of fibre mass m can be expressed with good approximation by the relation:

$$F = 4 \cdot m / (d \cdot \rho) = m \cdot \kappa_A \quad (6)$$

The value of the coefficient κ_A is determined by the weight mean of the fibre diameter and by the fibre density ρ for every kind of fibrous parent substance. This latter form of equation appears in all cases of physico-chemical processing in the textile, cellulose, and paper industries, and in the case of cotton, linter, and cellulose nitration.

In the process of gun-cotton (nitrocellulose) stabilisation, in which vestigial amounts of chemical compounds (mainly sulphuric acid ester and sulphonic compounds² causing its decomposition are removed, the equation form mentioned above changes as the result of agent milling aimed at developing the mass exchange surface. This fundamentally important operation had previously been carried out by 'paper hollenders' (and was named 'hollendration'). These machines were mostly destined for cellulose decomposition to fibres, similar to Jordan's cone paper mills, and this was why in the case of nitrocellulose processing the operation takes so long, demanded great amounts of energy, and was expensive. A decisive solution was the so-called 'Wrocławski mills' developed at PWP Pionki (the State Gun-Powder Enterprise in Pionki, Poland) in 1938 [1], which allowed a significant shortening of fibre length, and thus the development of the surface of mass exchange. The Germans manufactured these mills, known as 'Pionki Mühlen', in the Hipolit Cegielski - Poznań (HCP) Enterprise over the war period of 1940-1944³. They permitted the fibre length to be shortened

down to 0.1 mm and even less. According to H. Zenftman⁴, milling was accepted as good if the mean (by weight) fibre length of nitrocellulose fibres was within the range of two fibre diameters. The amount of 10 g of nitrocellulose milled in this way and stirred in 250 cm³ water occupied a volume smaller than 80 cm³ after sedimentation over a few hours. Under these conditions, the mean (by weight) mass exchange surface as a function of nitrocellulose mass could be calculated from the following, well-known equation [the end-surfaces of shortened fibres are added to F from (6)]:

$$F = m \cdot (1 + \pi/8) \cdot (4/(d \cdot \rho)) \quad (7)$$

As can be seen, this surface is 40% larger than the surface of those fibres which have not been cut; this operation has great significance for the increase in efficiency of the nitrocellulose stabilisation process and for its acceleration.

c) Form of the fibrous material agglomeration

The form of fibrous material agglomeration is of considerable importance. The fibres were dyed (in primary processes) in the state of free suspension in a liquid, and this method required a significant surplus in liquid in relation to the fibres. The fibrous form of matter has a tendency to the cohesion and creation of agglomerations in the liquid suspension which take the shape of flocks, skeins, bunches, and in extreme cases even of felted fleece. Mixing such a suspension only causes motion of the whole fibre agglomerations, whereas the liquid contained in the inner agglomeration space is in a state of relative rest. Then, mass exchange occurs by means of almost pure diffusion, which results in the process proceeding very slowly. An increase in the mixing intensity has only an insignificant influence on the relative liquid velocity in relation to the fibres, as thanks to the small differences in density between the fibres and the liquid, the fibres float together with the liquid; this occurs although inertia forces act in the whirling motion. The tendency of the fibrous parent substance to cohesion restrains the relative motion of the fibres in liquid and slows down the mass exchange in the processes under consideration.

The ability to absorb significant liquid amounts is a further particular feature of the fibrous form of the basic parent substance. Cotton fibres, linters, and the

fibrous form of cellulose (saturated with water) retain water of a mass more than ten times the mass of fibres, even after the water is dripped under the influence of gravitation forces⁵. Fibres also maintain this feature in the form of a suspension, immersed in the liquid, and thus not only when their densities are similar (as, for example, in nitrocellulose and nitration mixture) but also in those cases when the relative densities of fibre and liquid differ a little as for cotton, wool, and the majority of chemical fibres. For all different kinds of fibres a certain limit ratio (modulus) of the liquid amount to the fibre mass exists (while however not appearing to be very sharp), below which the fibrous suspension in its total mass has a relatively stable consistency (a quasi-gel consistency). When the modulus increases over its limit value, smaller or larger fibre agglomerations (which are relatively stable) appear floating in the liquid, the more unrestrained as the liquid modulus rises higher (compare also the statements in point e).

d) Forced liquid motion and the wall-surface layer

With the aim of accelerating mass exchange in the equipment designed for chemical processing of fibres, the fibres itself (in industrial textile processes) are positioned in vessels of various shapes, and the 'through' liquid motion (in relation to the agglomerated fibres) is forced by a pump. The liquid stream forced by the pump radically increases the relative liquid velocity (in relation to the fibres) inside the fibre agglomerations, which significantly decreases the thickness s of the wall surface layer. This thickness is directly proportional to the square root of the quotient of viscosity and liquid velocity:

$$s \sim \sqrt{(\mu/w)} \quad (8)$$

where:

μ - viscosity,

w - velocity of the liquid flowing around the solid body, and

\sim indicates the proportionality.

The liquid flow velocity (in those fibre agglomerations formed while enclosed in vessels) is small, within the range of one metre or even a part of one metre per second. However in relation to the relative liquid flow velocity caused by mixing the fibre suspension, which does not exceed 1 mm/s, it is up to a thousand times higher. This indicates without doubt the possibility of significantly decreasing

the wall surface layer⁷, and increasing the mass velocity of the reagents in relation to the fibre surface. However, a scientific and technical basis for further intensification of physico-chemical processes exists, especially for designing fully automated technological lines in a counter-current system. This will without doubt allow for a decrease in the exploitation costs, thanks to a decrease in the costs of labour, raw materials, water, and energy, and so in a decrease in environment pollution by the reduction of waste emission.

An effective forcing of the liquid motion in the process of cotton nitration was first achieved by means of the nitration method with the use of centrifugal machines over one hundred years ago [2]. The motion of the nitration mixture across the layers of the fibrous fleece nitrated was forced in these machines by inertia forces appearing as a result of the rotational movement of the centrifugal machine's basket. In this method, the maximum nitrogen number is achieved after only 10 to 15 minutes, that is, a time period at least two times shorter than in nitration machines with a mechanical stirrer, such as are used nowadays⁷.

e) Layer porosity

In estimating the conditions of liquid flow through agglomerated fibres (fibrous layers), a fundamental factor is porosity, a factor characterised by the un-dimensional quantity:

$$\Psi = 1 - m_w / (\rho_w \cdot V) \quad (9)$$

where:

m_w - fibre mass,

ρ_w - fibre density, and

V - the total volume of the space filled with fibres.

The porosity of the fibrous parent substance (which means the relatively free room between fibres) influences the resistance to liquid flowing through the fibrous layer, and so determines the liquid flow velocity in relation to the parent substance. Porosity depends on the degree of decomposition to fibres, the diameter and length of the elementary fibres, their elastic and rheological properties, the thickness of the fibrous agglomeration of the parent substance, and the pressure ('compression') acting on the surface of the agglomeration. This pressure can be exerted by the thrust of liquid flowing through the surface to the interior of the agglomeration or by the

earth gravity forces, or the centrifugal forces derived from the machine's rotating basket. A fibrous suspension in the liquid, of the same density as the fibre density, is characterised by the greatest porosity. Porosity is determined by the fibres' 'cohesion', which in this case means the fibre's ability to spontaneously create relatively consolidated agglomerations in a defined medium, for example in air, water, or the nitration mixture. The relative liquid flow velocity (similar to the liquid modulus) also influences the thermal conditions of the chemical reaction, which is especially important in the case of cellulose nitration. The influence can be exposed as heating or cooling. Even very small changes in the process temperature act on the shortening of the polymer (i.e. nitrocellulose) chain, and in the same way on the product viscosity. This in turn is to a significant degree a random phenomenon in parallel-flow processes, which makes the process under consideration difficult to control and requires a corrective, and expensive, water-thermal pressure processing (in an autoclave) of the nitrocellulose manufactured.

Determination of the porosity of the fibrous parent substance can be performed only by experiment. The dependency shown in Figure 1 presents the result of porosity tests of sulphite cellulose mechanically decomposed to fibres to the optimum form necessary to fulfil the requirements of the nitration process. The samples were formed from a cellulose water suspension deposited on a sieve at a water flow under pressure from 0.3, 0.6, and 1.2 m columns of water. The three measuring points and the initial point have been approximated by an exponential function of the type

$$Y = a - a \cdot \exp(-b \cdot \exp(-cx))$$

(The extrapolation for pressure values higher than the highest measured value is hypothetical; practical applications only have porosity for pressure values below a 0.6 m column of water).

Spun cotton fibres, linters, and cellulose create relatively consolidated suspensions (quasi-gels) up to a liquid content 13 to 15 times greater than the fibre mass. This multiplicity increases up to 25 for cellulose in a nitration mixture of 22% HNO₃, 69% H₂SO₄, and 9% H₂O, whereas for nitrocellulose in this same mixture it is within the range of 15.

The softened form of cellulose or linters destined for nitration (of dimensions resembling grains of rice or groats) consists the optimum form for processing. An undesirable or even destructive fraction is cellulose powder which creates a head on the surface of the nitration mixture, which only with difficulty is submitted to mix with the acids. Moreover, in a further phase of the process (after nitration), the heads slipped away with water which washes out the acids from nitrocellulose, and in the same way decreases the process' efficiency and pollutes the environment.

Linters are short cotton fibres obtained in the process of ginning cottonseeds after the separation of spun-grade fibres, whereas cellulose in sheets or bands consists of many wood cellulose fibres consolidated by cohesion forces into a shape of felted and porous sheets. The area of mass exchange is difficult to determine for such a fibrous form; it depends on the kind of the initial raw material (wood), and even on the conditions under which the tree grew and developed. However, it is possible to introduce a substitute surface according to (6) or (7), and in relation to this, to perform all the considerations required (see also point b).

Mass Motion in the Surroundings of Fibre

Mass motion is very similar to mass exchange during the bleaching and dyeing of fibres in the textile industry, in wood impregnation in the cellulose production, and in cellulose nitration. The cellulose nitration process is a most general case in which we have to deal with diffusion components in the form of liquid nitric acid, sulphuric acid, and water in ratios appropriate to obtain a specific product, which is nitrocellulose

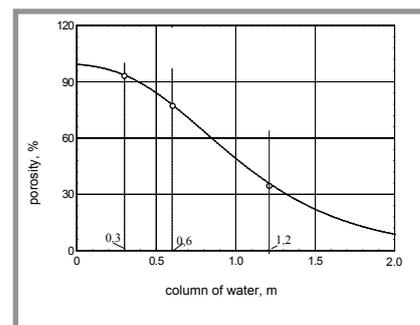


Figure 1. Porosity of sulphite cellulose decomposed to fibres mechanically.

of a required nitrogen number. In brief, the schema of mass motion is as follows: the diffusion components penetrate to the fibre surface from the liquid (which is in general stirred for fast equalisation of temperature and concentration of the components) through a liquid layer surrounding the fibre. The diffusion components permeate to the interior of the fibre, whereas water, which is formed in the reaction of nitric acid with cellulose, permeates in the opposite direction⁸. The resistance to this motion appears in the following areas:

- in the nitrated mixture itself, as an effect of reduction of the diffusion components in the fibre surroundings (which means a decrease in their concentration);
- in the tranquillised liquid layer (film) surrounding the fibre (the mean by weight diameter of the wall-surface layer is more than three times greater than the fibre diameter)⁹;
- on the fibre surface (at the contact of the surface with the wall-surface layer); and
- inside the fibre (in the solid phase).

The decrease in the resistances mentioned above results in economical advantages caused by a decrease in the dimensions of the equipment for conducting the process, a decrease in the manufacturing area, a shortening of the process period, and the creation of opportunities for performing the counter-flow process.

The motion of the component in liquid is in general a function of the liquid's turbulences, and is described by the Reynolds number. To achieve an increase in the component motion intensity, at a liquid viscosity defined for the existing conditions, the relative velocity of the moving liquid particles should be increased, which in fact agrees with intuition.

The motion of the component in the tranquillised liquid layer surrounding the fibre (the wall-surface layer) and the decrease in concentration of the component at the fibre surface are very complex functions which depend on many factors. The following relation of the criteria of similarity (sufficiently for these considerations) describes this phenomenon:

$$Sh = Re^A \cdot Sc^B \quad (10)$$

where:

Sh - the Sherwood number

$$Sh = h \cdot d / D \quad (10a)$$

k - the coefficient of mass penetration, in m/hour¹⁰,

d - the geometrical parameter (a characteristic linear measure) in m; and

D - the diffusion coefficient, in m²/hour, A and B - constants.

The k coefficient is directly related to the α_m coefficient specified earlier (4):

$$\alpha_m = k \cdot \gamma, \text{ kg/m}^2\text{hour} \quad (10b)$$

whereas the diffusion coefficient D is directly related to the afore-mentioned δ (3) for small concentrations:

$$\delta = D \cdot \gamma, \text{ kg/m hour} \quad (10c)$$

At higher concentrations the phenomenon is more complex but its character remains the same.

The Reynolds number from equation (10) is described by:

$$Re = w d \rho / \mu \quad (11)$$

where:

w - agent motion velocity, m/hour;

D - geometrical parameter, m;

ρ - density, kg/m³; and

μ - dynamic viscosity, kg/m hour.

The Schmidt number is described by:

$$Sc = \mu / (\rho \cdot D) \quad (12)$$

By substitution we achieve:

$$k_m d/D = (w d \rho / \mu)^A \cdot (\mu / (\rho D))^B \quad (13)$$

where k_m is analogous to α_m .

From this relation, it is directly apparent that the process designer and equipment constructor only has the possibility to change the geometrical parameter d and the flow velocity w , as the quantities μ , ρ , and D are determined and constant under the existing technological conditions. By denoting these quantities as 'constant', equation (13) takes the form:

$$k_m = const \cdot w^A \cdot d^{A-1} \quad (14)$$

From experience it is known that the exponent A is smaller than one, and thus:

$$k_m = const \cdot w^A / d^{1-A} \quad (14a)$$

A conclusion is evident: an increase in the process intensity can be achieved only by an increase in the velocity w and a decrease in the geometrical parameter d .

The premises discussed formed the basis for evident intensification (up to 15 times) of fibre dyeing processes in the textile industry.

This conclusion, drawn as a result of the analysis carried out on the basis of the permissible simplifications (from the point of view of a qualitative analysis, and usable for the process modelling), agrees with the previous conclusion connected to mass motion in the liquid phase. The constructor can resort to only two measures for decreasing the resistance in mass motion:

- increasing the mixing intensity (increase in the relative parent substance's velocity), and
- decreasing the dimensions of the equipment designed for mass exchange.

Mass permeation inside the fibre depends on the designer only to a small degree. It is determined by properties of the diffusion agent, the fibre, and ultimately the inertia liquid.

The reagent properties are the subject of chemists' investigations. Regarding the process of cellulose nitration, for example, the designer has at his disposal data based on the experience of process engineers, which data are fully sufficient for designing the modules of model equipment (such as equipment with a yield of 200 kg cellulose per hour, which corresponds to about 320 kg of nitrocellulose per hour). This in turn, after the tests performed, allows a full technological line to be designed, and what is more, for its automation after successive modernisation stages. Such conduct allows us to achieve important economic advantages as well as a significant increase in the quality of the product.

The relation (14a) presented above can be used by designers of apparatuses in a simple way, as a significant instrument for intensifying the process and changing its scale. If we denote by indexes the quantities of two process scales (e.g. 1 for the 'model', and 2 for the 'industrial' scale) and take the ratio of equation (14a) for both scales, we achieve the relation:

$$\chi = (w_2 / w_1)^A \quad (15)$$

which is the intensification coefficient of process '2' in relation to process '1' resulting from the change of velocity from the value w_1 to w_2 , and by accepting that

the geometrical parameter d will not be changed in either of the processes.

The development of machines and apparatuses for the physico-chemical processing of fibres in the textile industry, which has been constantly underway since the mid-1950s, has been in full agreement with the conditions and conclusions which arise from this analysis of the relation between the process intensity and the development of equipment and its design methods. An opposite situation is visible in the nitration process, although the experience attained in the textile industry may be utilised for the significant modernisation of machines, apparatuses, and installations for nitrocellulose manufacture - though of course by means of appropriate design of apparatuses and installations adapted to processes with the use of other reagents.

All the considerations and theoretical premises considered in this paper¹¹ can be applied to all operations of mass exchange in which fibre is the main parent substance, especially to the following:

- processes of chemical and physico-chemical processing of fibrous materials, such as washing, bleaching, dyeing, impregnation, and improving;
- wood impregnation in cellulose production;
- cellulose nitration and nitrocellulose stabilisation, and also its boiling; and no less important,
- purification of wastewater after chemical processing, including that which includes alkali from chemical reactions, nitrocellulose, and remains of nitration acids washed out.

When considering the possibilities of a scientific relation to the problems of designing and constructing new machines and apparatuses destined for cotton nitration and nitrocellulose stabilisation as analysed in this work, it should be appreciated what kind of difficulties may appear in the foreseen future. These difficulties arise from the common traditionalism of managers and engineers, to whom the Max Planck 'rule' can be applied:

"The scientific truth very rarely gains esteem, most often it capture opponents: just as it very rarely happens that Saul is transformed into Paul. In reality the opponents die out step by step, and the new generation becomes accustomed to new solutions from the very beginning."

Conclusions

- The physico-chemical processing of fibrous materials is a scope of knowledge which has been insufficiently scientifically elaborated until now, and requires further development, as thanks to such work considerable advantages and economic savings in fibre processing can be achieved (to which the circumstances are nowadays conducive, as the old generation retires and slowly dies out).
- The industrial installations which have hitherto existed in the industry, and the processes they carry out, can be used for the modelling of new installations and processes by means of applying the approach to this subject presented in this paper. This also creates an opportunity to modernise the existing installations and intensification of processes, and also allows us to minimise the risks of such undertakings, especially in such a case when the chemistry of the processes is well-known and need not be changed by the first applications of new solutions.
- The starting point of a new process can be the process and equipment which exists at present, and which is an excellent 'research model of the previous (initial) generation'. The tools for transmitting test results and process parameters into the new installation are the similarity criteria generally known and described in this analysis. Such a philosophy demands considerably smaller financial outlays (in particular cases, even relatively insignificant) and shorter time periods for developing processes and designing installations than in the case of fundamental research work which would not be based on the experience of technologists and experimenters.

Footnotes

1. The term 'natural experiment' was introduced by Professor Marian Chwalibóg, the late professor of the Technical University of Łódź, for investigations conducted with the use of industrial lines during normal exploitation.
2. Cellulose compounds, in which sulphur is directly connected with a carbon atom,

are especially burdensome in the stabilisation process.

3. These type of mills are working in Pionki up to the present day.
4. Unpublished investigation carried out at the PWP Pionki works.
5. A similar feature (but not as intensive) could be stated by the authors for hydrophobic polypropylene fibres of a diameter of 0.1 mm, which in the state of agglomeration absorb water to an amount of about 120% of the fibre mass.
6. The theory of the wall-surface layer is elaborated in connection to the liquid flow around simple body shapes, such as plate, sphere, ellipsoid, cylinder, as well as cones and surfaces which are parts of these bodies. Up to now, no good mathematical description exists of a generalised theory which would consider bodies of irregular shape and agglomerations, e.g. fibrous, such as those which appear under the conditions of the problem analysed.
7. The method described was given up, despite its high process efficiency, because its conduct was accompanied by troublesome manual operations and frequent occurrence of ignitions or even explosion of the gun-cotton; one of the authors of this article was present during such an incident in 1937.
8. The motion created in the reaction of water in the direction opposite to the direction of diffusion of the components does not take place in other cases, for example if the reaction is additive as for dyes which react with cellulose, or when the reagent is considerably diluted.
9. According to investigations carried out by the authors, which have not hitherto been published.
10. The units which characterise the quantities in this paper are by intention units used in technological design, and not SI units.
11. The starting point of this study was the research works carried out at the former PWP Pionki (Pionki State Gun-Powder Mill) by W. Czerwiński, J. Wrocławski, and H. Zenftman, related to cellulose nitration and nitrocellulose stabilisation; these research works have been further updated up until the present time.

References

1. Wrocławski J., Polish Patent 26464, 1938, PWP (State Gun-Powder Enterprise in Pionki), Poland.
2. Selwig, Lange, German Patent 64447, 1891.

Received 30.06.2003 Reviewed 08.09.2003