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Institute for Synthetic Alcohols and Organic Products, Moscow

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Synthesis of Technical Tanning Agents

Ya.P.Berkman

The review gives data mainly on Soviet investigations on the preparation and application of synthetic tanning agents, comprising auxiliary syntans and substitutes for vegetable tannins. A detailed account is given of the processes used in the synthesis of Soviet heavy-duty syntans and some information on the production of substitute syntans abroad. The bibliography contains 83 references.

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I. INTRODUCTION

Since the earliest times tanning agents, found in the bark, wood, leaves, and roots of various plants, have been used for the production of leather. The structure of these substances, which are known generally as "tannins", was elucidated as a result of the large amount of work done during the second half of the nineteenth century and the beginning of the twentieth century. All natural tanning agents are derivatives of polyhydric phenols, and are divided into two groups: the chief structural unit of hydrolysable tannins is digallic acid, which forms esters with hexoses; non-hydrolysable tannins are based on catechol units linked together either directly or through carbon atoms [1].

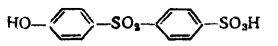
At the same time as the investigation of the structure of vegetable tannins, and directly connected with it, work was also done on the synthesis of tanning agents with the above main structural units as starting materials. Such syntheses were undertaken by Schiff, Baeyer, Fischer, Melau, and others, who by various methods obtained condensation products of arenepolyols and hydroxybenzoic acids.

The work of Schiff is of especial interest for the history of synthetic tanning agents. Having obtained digallic acid from gallic acid by the action of phosphoryl chloride, he applied this method to pyrogalloisulphonic acid and hydroxybenzenesulphonic acid [2], and assigned to the products the formulae

$$C_6H_2(OH)_3-SO_2-O-C_6H_2(OH)_2-SO_3H,$$
$$C_6H_4(OH)-SO_2-O-C_6H_4-SO_3H.$$

While differing from digallic acid in composition, these compounds showed some analogy with it in molecular structure: they contained phenolic rings linked by ester groups (-CO.O- or $-SO_2.O-$) and one of the rings contained an acidic group (-COOH or $-SO_3H$). Both compounds possessed tanning properties, and underwent all the reactions characteristic of vegetable tannins.

Schiff also obtained a tanning agent [3], probably hydroxyphenylsulphonylbenzenesulphonic acid



by dehydrating hydroxybenzenesulphonic acid at a high temperature.

These compounds obtained by Schiff must be regarded as direct precursors of modern synthetic tanning agents.

The history of modern industrial synthetic tanning agents, usually termed syntans (synthetic tannins), began in 1911, when Stiasny made a patent application covering the production of tanning materials by the condensation of hydroxybenzenesulphonic acids with formaldehyde [4,5]. Synthetic tanning agents have come a long way. More than a thousand patents have been issued on processes for their production, while the total number of brands manufactured in various countries reaches two hundred.

Synthetic tanning agents can be divided into two main groups—"light" and "heavy"—from the point of view of leather technology. Those of the first group possess weak

forming and filling power. They do not confer the required commercial properties on leather, but their use together with vegetable extracts or mineral salts has a substantial effect on the tanning process and on the properties of the leather. In conformity with this they are usually termed auxiliary.

Synthetic tanning agents of the second group approach vegetable tannins in their tanning action, and several of them even surpass the latter. Therefore the "heavy" syntans can replace vegetable extracts either completely or to a considerable extent. Hence the name substitute syntans.

Only very few synthetic tanning agents are individual compounds. Most of them are polydisperse mixtures of oligomers. Their tanning ability depends both on the chemical type and on the physicochemical characteristics of the product (degree of polycondensation, degree of dispersion). The range of possible variation in physicochemical characteristics differs in different chemical types, so that the range of technical properties with respect to leather (tanning action) which is possible for them also differs. From sulphonic acids of aromatic hydrocarbons, for example, only auxiliary tanning agents can be obtained, whereas hydroxybenzenesulphonic acids enable syntans to be prepared with any properties–from light auxiliaries to complete substitutes.

II. AUXILIARY SYNTANS

The group of auxiliary synthetic tanning agents was the first to appear, remained the only group for twenty years, and until now has been the most widely used in foreign countries.

Brands belonging to this group are used for two main purposes: (1) they are combined with vegetable extracts to improve the dissolution of the latter, accelerate tanning, lighten the leather, and protect the tanning solutions from fermentation and putrefying processes, the partial replacement of vegetable tannings being of second importance; and (2) they are combined with a mineral tannage (mainly chrome) to thicken the leather, enhance the plasticity of the fare side, bleach the skin, and prepare it for dyeing and finishing operations.

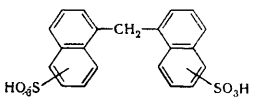
A. Auxiliary Syntans for Use with Vegetable Tanning Agents

This category was first realised in production as the synthetic tanning agent Neradol D, manufactured by the Badische Anilin- und Sodafabrik in conformity with Stiasny's patent. The idea underlying the process was that, in order to obtain an economically acceptable product, possessing the three main chemical and physicochemical characteristics of vegetable tannins–phenolic nature, a large molecule and solubility in water–the most accessible starting material was phenol and its homogues, the molecule was enlarged by condensation with formaldehyde, and solubility could be ensured by introducing a sulpho-group.

Neradol D was dihydroxydiphenylmethanedisulphonic acid. It precipitated gelatin from solution, and showed some resemblance to vegetable tannins in its qualitative reactions, but it differed sharply from them in its tanning power. It was not an analogue of vegetable tannins, but a representative of a new type of tanning material, giving a special kind of leather–light, smooth, and not compact–unsuitable for those purposes for which vegetable-tanned leather is used. Without being a complete substitute, Neradol D was, however, useful for combining with vegetable extracts: it lightened the leather, and prevented the formation of precipitates in the tanning solutions, which economised the consumption of tannins.

The industrial realisation of Stiasny's patent stimulated the development of analogous processes for obtaining tanning agents, and during the following years it was established that the presence of a hydroxy-group was not necessary for an aromatic sulphonic acid to exert a tanning action, this being possessed also by sulphonic acids of hydrocarbons and of certain heterocyclic compounds.

The first patent on syntans from hydrocarbons was issued[6] in 1916. The product was a mixture of naphthalene-1- and -2-sulphonic acids condensed with formaldehyde



and was named Neradol ND. The naphthalene syntan possessed poorer tanning power than the phenol syntan, but differed little from it in the effect achieved on being combined with vegetable extracts.

Neradol ND was succeeded by Ordoval, a product resulting from the sulphonation of mixtures of carbazole and anthracene, crude anthracene, or "anthracene residues".[7] This syntan, in contrast to the Neradols, possessed no brightening power, but in its tanning action even somewhat surpassed Neradol ND.

The absence of special advantages in the phenolic syntan and its relative dearness pushed it into the background.

The blockade of Germany during the First World War led to a shortage of tanning materials, and at first syntans were widely used to replace them. The large-scale application of syntans and the ignorance of their specific features and differences from natural tannins resulted in wholesale damage to leather, caused by the hydrolysis of collagen. The consequences of this were very unfavourable for syntans. By 1923 the manufacture of Neradols and Ordoval had fallen to a very low level. The use of artifical tanning materials as replacements for vegetable tannins almost ceased in the West for more than a decade[8].

During this period, in which interest in synthetic tanning agents dropped sharply in the West, the present Reviewer together with Kiprianov and Tolkachev began investigations in this field at the Ukrainian Institute of Applied Chemistry in Kharkov. At that time a large quantity of tanning extracts were imported into the USSR from abroad, and therefore even a partial replacement of vegetable by artificial tanning agents would have been of great economic value. In addition, the industrial manufacture then of new chemical products involved serious difficulties, and the contingency depended on the choice of raw material and the necessary equipment. The German commercial brands were soon identified and data were obtained which might serve as a control in our experiments[9].

Crude anthracene– a technical mixture of polycyclic aromatic hydrocarbons and heterocyclic compounds, which is precipitated from anthracene oil on cooling–was selected as the most accessible starting material. The composition of crude anthracene is variable: the solid part constitutes ~70%, and contains on the average 60% of phenanthrene, 20% of carbazole, and 15% of anthracene[10]. The first two components are of great value for the production of tanning materials. They are considerably more readily sulphonated, and give clearer solutions. Increasing the content of anthracene in the mixture makes it difficult to

obtain a product of satisfactory quality. Enriched anthracene must be regarded as, in general, unsuitable for the synthesis of tanning agents.

Crude anthracene was sulphonated with 150% of 92% sulphuric acid at 120°C for 5 h, with formation of a mixture of sulphonic acids of equivalent weight 210–220, which corresponds approximately to equal proportions of mono- and di-sulphonic acids. Sulphonation is accompanied by some resinification of the product with liberation of sulphur dioxide. The addition of a small amount of naphthalene helped to stabilise the solution [11]. Condensation of the sulphonated mass with formaldehyde, which is necessary with hydroxybenzene- and naphthalene-sulphonic acids, proved to be unnecessary, the sulphonic acids of tricyclic compounds exhibiting sufficient tanning action even without condensation. However, this process led to some improvement in the properties of the tanning agent, more rapid dyeing of the leather, and considerable lightening. The optimum effect was achieved with a small quantity of formaldehyde, 0.1–0.2 mole per mole of anthracene (compared with 0.5 mole of aldehyde per mole of phenol or naphthalene). In order to diminish the acidity the product was partly neutralised with sodium carbonate. In its final form it was a mixture of sulphonic acids, their sodium salts, and sodium sulphate.

The above process was put into practice at the Rubezhanskii Chemical Works with the production of two brands of tanning agents, AN (anthracene normal) and AK (anthracene condensed)†. They were widely used in the leather industry, especially the AN brand, which found application up to the end of the 1950s in the manufacture of sole leather.

In order to improve the colour of leather obtained by tanning with anthracene syntans, the sulphonated mass was oxidised with sodium hypochlorite, chlorine, and dichromate. Oxidation produced considerable clarification of the tanning solutions, but had little effect on the colour of the leather. However, provided that the sulphonated mass had first been condensed with formaldehyde, oxidation gave a very favourable effect [12]. Production of the tanning agent AKO (anthracene condensed, oxidised) involved the operations of sulphonation of crude anthracene, condensation with a small quantity of formaldehyde, neutralisation, crystallisation of sodium sulphate, making alkaline with caustic soda, oxidation with chlorine, and acidification with sulphuric acid. This tanning agent conferred a light, natural colour on the leather, but the complexity of the technique prevented its introduction into industry.

Oxidation with dichromate provided a considerably simpler method of obtaining the tanning agent. After condensation with formaldehyde the sulphonated mass was treated with a small quantity of water to lower the viscosity, and was three-quarters neutralised with sodium carbonate. The product was then oxidised with a concentrated solution of sodium dichromate, in amount such that all the remaining acid was neutralised by the bases formed on reduction of the dichromate [13]. The dry tanning agent comprised 30% of chromium sulphonate, 40% of sodium sulphonate, and 30% of sodium sulphate [14].

The tanning action of this syntan (Bestan AS) was considerably greater than that of the anthracene brands, since it was accomplished not only by the anion of the sulphonic acid but also by the chromic cation. The leather obtained was well formed and was stable to temperature. But the most valuable aspect was the safety in use of Bestan AS. In contrast to the anthracene brands, this tanning agent contained no free sulphonic acids. The acidity of its solutions was due solely to hydrolysis of the chromium salts. This kept the active acidity at a relatively low level, and conferred a buffer stability on the solutions, thereby preventing the possibility of hydrolysis of the collagen with weakening of the fibre [14].

Manufacture of Bestan was begun by the Rubezhanskii Chemical Works in 1930, and production soon reached several thousand tons per annum.

In 1934 the building was completed at Konstantinovka (Donets Region) of a factory for the manufacture of synthetic tanning agents. This works' range included five brands of syntans and an auxiliary type–Bestan AS, Bestan N (from naphthalene), the anthracenic AN and AK, and the naphthalenic NK–among which AK and Bestan AS were used for the accelerated tanning of Russia leather by a syntan–vegetable process, in which a considerable proportion of vegetable tannins had been replaced by synthetic tanning agents. The practical value of the brands AN and NK was determined mainly by their dispersing action on vegetable tannins. Their application to the manufacture of sole leather considerably improved the solubility of the vegetable extracts, stabilised the solutions [15], and accelerated the tanning process. Syntan NK has been widely used for this purpose up to the present time.

B. Auxiliary Syntans for Special Purposes

Other conditions for synthetic tanning agents arose in the West during the period following the First World War. As has already been stated, their use in Germany as substitutes for vegetable extracta almost completely ceased. However, specific features of these products maintained interest in their use for special purposes in the manufacture of both vegetable-tanned and chrome-tanned leather. As a consequence of this, new processes continued to be developed in the West for obtaining synthetic tanning agents. These processes were essentially variations on known methods. They can be divided into several groups: (*a*) the range of starting materials was expanded to naphthalene homologues, tetralin, benzylnaphthalene, naphthols, aromatic hydroxy-carboxylic acids, ethers of phenol with aliphatic alcohols, and esters thereof with aliphatic acids; (*b*) substituents–chloro-, nitro-, and amino-groups–were introduced into the aromatic rings; (*c*) various substances–acetaldehyde, paraldehyde, acetone, carbohydrates, sulphur, sulphur monochloride–were condensed with naphthalene- and hydroxybenzene-sulphonic acids; and (*d*) the sequence or the conditions of the operations–condensation under pressure, condensation at the instant of formation of the aldehyde (by passing acetylene into the sulphonated mass in the presence of a mercury salt), condensation of aromatic compounds by means of an aldo-group or an alcoholic group present in them, condensation before sulphonation, the introduction of substituents before or after sulphonation, the sulphonation of a compound containing an aldo-group or an alcoholic group and subsequent condensation with an unsulphonated compound–were varied.

These and similar modifications, described in European and American patents, are summarised in Bergmann and Grassmann's encyclopaedia of the leather industry [16]. It must be said that only a few of them were used industrially.

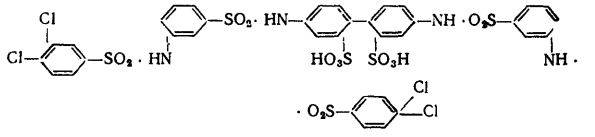
By contrast, in the manufacture of special-purpose auxiliary syntans based on hydroxybenzene- and naphthalene-sulphonic acids, various secondary procedures came into wide practical use, with the aim of improving the properties of the tanning agent, intensifying some particular

† The name "anthracene" is, of course, conventional indicating that the product has been obtained from crude anthracene.

feature in relation to a definite purpose, or increasing convenience in use. Among such procedures are removal of the inorganic portion, control of acidity, neutralisation with volatile bases (ashfree state), the addition of various salts (sodium chloride, sodium hydrogen sulphate, or potassium oxalato-aluminate, or -chromate, or -titanate) addition of organic acids (acetic, formic, oxalic, lactic), addition of preparations to prevent discoloration by iron ions (Trilon B)[17]. The differences between many brands of auxiliary syntans, even those manufactured at the present time, reduce to the use of particular supplementary procedures of the above type.

Special difficulties were presented by the synthesis of tanning agents which would make it possible to obtain a pure white leather fast to light, in particular a leather which would preserve its natural grain and colour (e.g. the leather of reptiles).

A great advance on these lines was represented by tanning agents proposed at the beginning of the 1930s, which contained several aromatic rings linked by sulphonamide groups[18]. It was found that the $-SO_2.NH-$ group, like a hydroxy-group in an aromatic ring, was a "tannophore", and a compound containing three or four such groups in the molecule possessed active tanning power. An industrial tanning agent of this type, manufactured in Germany by the firm IG. Farbenindustrie AG. under the brand name Tannigan LL, was identified and reproduced[19]. It was prepared from benzidine-2,2'-disulphonic acid by acylation with *m*-nitrobenzenesulphonyl chloride, followed by reduction of the nitro-group and further acylation with dichlorobenzenesulphonyl chloride, which yielded:



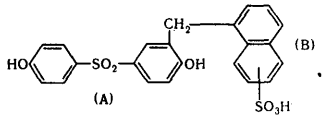
This syntan gave a white leather highly resistant to light, and also possessed considerably greater forming power than any other auxiliary tanning agent known at that time. It was also of theoretical interest, since it was the first individual, crystalline tanning agent. Brands of tanning agents of polysulphonamide type are still being manufactured in the Federal Republic of Germany.

Colourless syntans, stable to light and based on phenol, were also proposed, A peculiarity in their method of preparation was that the intercyclic methylene link formed by condensation with formaldehyde was replaced by other groups, such as $C(CH_3)_2$, $CH_2.NH.CO.NH.CH_2$, and SO_2. This resulted in a considerable diminution in the oxidisability of the condensation product compared with diphenylmethanediol, and on storage the leather preserved a light colour for a long time.

An isopropylidene link is formed by condensing the hydroxybenzenesulphonic acids with acetone[20], and a ureylenedimethylene link by simultaneous condensation with formaldehyde and urea[21] or by condensation with bishydroxymethylurea[22]. The use of urea to lighten leather was widely introduced into practice, and at the present time is often employed in the synthesis of tanning agents belonging to various chemical types.

Among the above variants, however, the use of aromatic hydroxy-compounds in which the rings were linked through a sulphonyl group acquired the greatest value, primarily bis-*p*-hydroxyphenol sulphone, which became one of the most important intermediates in the synthesis of tanning agents. Syntans based on bishydroxyphenyl sulphone are prepared in three ways–(*a*) sulphonation followed by condensation with an aldehyde[23], (*b*) simultaneous condensation with an aromatic sulphonic acid and formaldehyde[24], and (*c*) sulphomethylation and condensation with formaldehyde[25]–brands for white leather being produced mainly by the latter two methods.

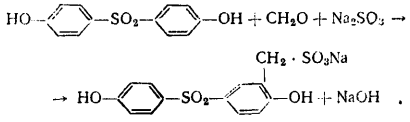
The purpose of simultaneous condensation of the sulphone with naphthalenesulphonic acid is to link the two molecules through a methylene group, with formation of a water-soluble product:



A and B condense in the various permutations so that the final product is a mixture of $A.CH_2.A$, $B.CH_2.B$, and $A.CH_2.B$, together with a certain amount of unchanged A and B. Reich[26], in an investigation of the analogous product of the simultaneous condensation of bis-*p*-hydroxyphenyl sulphone and 6-hydroxynaphthalene-2-sulphonic acid with formaldehyde, showed that only 50% of the sulphone gives a mixed condensation product, the remainder going into colloidal solution as a consequence of the protective action of the sulphonic acid.

Tanning agents of this type, obtained from pure starting materials (sulphone and naphthalene), yield a white leather having a plastic surface layer. The conditions for carrying out the synthesis were studied, and the dependence of the tanning action–the increase in the forming and filling power–on the relative proportions of sulphone and naphthalenesulphonic acid was established[27].

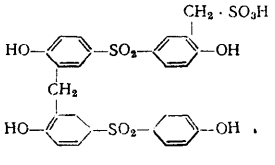
The method of sulphomethylating (or ω-sulphonating) a sulphone consists in the simultaneous condensation of the sulphone with formaldehyde and with sodium sulphite or a mixture of the sulphite and the hydrogen sulphite. This involves the introduction of a sulphomethyl group into the ring:



In the presence of excess of the aldehyde, ω-sulphonation is accompanied by condensation of the sulphone with the aldehyde[28].

As in the co-condensation of bishydroxyphenyl sulphones with naphthalenesulphonic acid and formaldehyde, sulphomethylation yields products which surpass the average of auxiliary syntans in their tanning action. The solubility of a product and its tanning action are greatly dependent on the relative proportions of sulphone, sulphite, and formaldehyde.

A detailed investigation of the condensation of bis-*p*-hydroxyphenyl sdulphone with formaldehyde[29] led to the isolation in crystalline form of an intermediate hydroxymethyl derivative, and it was shown that, with molar proportions of sulphone, sodium sulphite, and formaldehyde of 1.10 : 1.0 : 0.5, the chief product is a tetracyclic compound containing one sulphomethyl group[30]:



The advisability was also established[31] of conducting the process in two stages: (*a*) the sulphone was condensed with formaldehyde in the presence of small amounts of the sulphite as catalyst; and (*b*) sulphomethylation was effected with formaldehyde and the sulphite present in equimolecular quantities. This process was used for several [years?] to produce in an experimental plant Tanning Agent SB (Sulphone White), which was used by the works as a levelling agent in the dyeing of chrome leather in pale colours.

III. SYNTANS USED AS SUBSTITUTES FOR VEGETABLE TANNINS

A. Development of Methods for the Production of Substitute Syntans in the USSR

During the middle 1930s synthetic tanning agents of a novel type appeared in Germany under the name "Tannigans extra". Leather obtained by tanning with these syntans was closely similar to vegetable-tanned leather in physical properties and in yield by volume and weight. This permitted them to be used as complete substitutes for natural tanning materials.

The patent literature of those years revealed no fundamentally new methods for the synthesis of tanning agents, and the mode of production of Tannigans extra remained unknown, although papers in the periodical literature indicated that the new syntans were distinguished from the previous (auxiliary) syntans in starting materials, the functional groups responsible for their tanning action, and the active acidity of the solutions[32].

From this it must be supposed that the German Tannigans extra were weak acids: i.e. unlike the auxiliary syntans they could not be classed as aromatic sulphonic acids. This formed the starting point for the work of Konovalenko et al. on the preparation of a tanning agent free from sulpho-groups condensing resorcinol with acetaldehyde[33]. Their product, to which the name "Rezotan" was given, possessed good tanning power, but its industrial production was prevented by its high cost.

At the same time an investigation was being made at the Ukrainian Institute of Applied Chemistry into the possibility of obtaining substitute syntans of the sulphonic-acid type by varying the conditions under which the individual stages were conducted and varying the quantitative proportions of the reactants[34]. This work was based on an observation made in an attempt to increase the organic content in the anthracene brands by introducing a phenolic, Novolak resin into the sulphonated mass. It was supposed that excess of sulphuric acid present in the sulphonated mass, although at a low concentration, would be able to sulphonate a certain amount of the resin, with a consequent diminution in the organic content of the tanning agent, and an increase in the so called quality–the content of adsorbable material.

It was found that the resin was sulphonated to a very slight extent, but a homogeneous product, forming quite stable colloidal solutions, was obtained by stirring it with the sulphonated mass and heating[36]. By means of such dispersion it proved possible to bring into a soluble state up to 100% of resin based on the quantity of crude anthracene in the sulphonated mass. With increase in the quantity of resin the stability of the colloidal solution diminished: the quantity of resins which could be salted out by electrolytes increased. This was accompanied by increase in the volume yield and the tanning coefficient of the leather [(Table 1)]: i.e. its properties approached closer and closer to those of vegetable-tanned leather.

A similar result was obtained with naphthalenesulphonic acids condensed with formaldehyde. Thus recourse to other chemical types was not necessary in order to obtain heavy-duty synthetic tanning agents, possessing fundamentally new technical properties towards leather, for this could be accomplished within the limits of the same type of aromatic sulphonic acids as for the production of light duty, auxiliary syntans. It was achieved by increasing the organic loading on the sulpho-group by intermolecular bonding of a sulphonic acid with a phenolic resin of low degree of polymerisation.

Table 1.

Phenolic resin, % on crude anthracene	Vol. yield of leather, % on hide	Tanning coeff. of leather
0	165	20
30	222	25
50	251	31
100	292	55

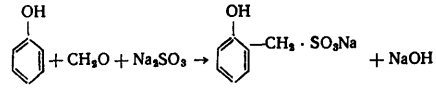
The dispersion of a phenolic resin in the sulphonic acids raised their tanning action to a higher level: i.e. it "improved" the tanning agent, as it were. Hence our brand letters–AO and NO–for the new anthracene and naphthalene tanning agents.

A very favourable result was obtained by dispersing a phenolic resin in ligninsulphonic acids (concentrates of waste sulphite liquors from the manufacture of cellulose)[34]. These liquors were suggested for use in leather production as early as the end of the nineteenth century, and were employed in industry, after preliminary purification, under the name of sulphite–cellulose extracts. However, their very feebly developed shaping power allowed them to be used only as an ancillary product, predominantly as a filler to increase the density of the leather and raise the yield by weight. Numerous attempts to improve the tanning power of sulphite–cellulose extracts produced only a very insignificant effect[37].

The dispersion of a phenolic resin in sulphite concentrates led, as with aromatic sulphonic acids, to a series of syntans the later members of which were not inferior to vegetable tannins in their tanning ability. These improved sulphite–cellulose extracts were denoted by the letters LF (lignin–phenolic).

The results of applying the same method to condensed hydroxybenzenesulphonic acids were very significant for subsequent work. Dispersion of a phenolic, Novolak resin in them yielded purely phenolic syntans, which exhibited a gradual change in tanning ability from the auxiliary type to well defined full substitutes[38]. This suggested the possibility of obtaining a similar series of phenolic syntans not by dispersing but by directly sulphonating the phenolic resin with a diminished quantity of sulphuric acid, so that only a proportion of the phenolic resins could undergo sulphonation, the proportion decreasing as the molar ratio of sulphuric acid to phenol was decreased. The part of the resin which had not been sulphonated would then be dispersed in the sulphonated product. This hypothesis was confirmed. Soluble products could be obtained even with a molar ratio of monohydrate to phenol in the resin of 0.15 : 1.00.[39] The corresponding series of tanning agents proved to have the widest range of variation in technical properties towards leather. The series was denoted by FT (phenolic heavy)[35].

Decreasing the ratio of sulphonating agent to the phenol, which was used to obtain the FT series of syntans, was applied also to another method of obtaining synthetic tanning agents–the condensation of phenols with formaldehyde and sodium sulphite, resulting in sulphomethylation of the phenol (termed also ω-sulphonation).



This process, known since the early years of the appearance of industrial syntans [40,41], acquired no practical value, since it yielded tanning agents of the same light type as did the condensation of hydroxybenzenesulphonic acids with formaldehyde. When the quantity of sulphite was diminished and that of the aldehyde increased, products were obtained which were typical heavy syntans, denoted by the letters FB (phenolic with a sulpho-group in the side-chain).

Thus by the prewar period synthetic methods had been developed which yielded a number of Soviet brands of synthetic tanning agents, making it possible, depending on the type of leather production, to replace vegetable extracts either completely or to a considerable extent [35]. Since 1938 these new brands have been manufactured in experimental production batches, and have been tested with positive results on various types of leather. The potentially most useful were the purely phenolic tanning agents of the FT series and ligninsulphonic concentrates improved with a phenolic resin (LF series). By combining them it was possible to obtain, without the use of vegetable extracts, both stiff and supple types of leather (sole leather and Russia leather) having normal physicomechanical properties.

B. Processes employed in the Synthesis of Soviet Heavy-duty Syntans

1. PREPARATION OF PHENOLIC RESIN

In Stiasny's original patent two methods were proposed for obtaining condensation products of hydroxybenzenesulphonic acids with formaldehyde, which differed in the sequence in which the operations of sulphonation and condensation were carried out. No distinction was made between them in the patent, and the first tanning agent, Neradol D, was obtained by sulphonating phenol and then condensing with formaldehyde. Subsequently Wolesensky [42] noted peculiarities in the products obtained by these methods, and pointed out that the second method (preliminary condensation of phenol with the aldehyde) yields a well filled leather, but involves difficulties in sulphonation and the possibility of "charring" of the resin.

A comparative study of the two alternatives has confirmed the difference in properties of the leather pointed out by Wolesensky, but no difficulty was found in the sulphonation. On the contrary, prelimary condensation had a decided advantage over subsequent condensation also in conducting the synthesis. With the stoichiometric proportion of sulphuric acid stable solubility for the resin was reached considerably more rapidly and at a less elevated temperature. With smaller amounts of acid a soluble condensation product could not be obtained at all from the sulphonated phenolic mass. In the synthesis of heavy-duty phenolic tanning agents, therefore, preliminary condensation of the phenol with aldehyde is of very great value.

The condensation of phenols with formaldehyde has been studied thoroughly, and its mechanism is known. The preparation of synthetic tanning agents requires a resin of Novolak type: i.e. condensation should be conducted in acid medium. A resin obtained by alkaline condensation leads to complications in subsequent sulphonation, owing to the presence of hydroxymethyl groups and the consequent tendency to thermosetting. In the presence of concentrated sulphuric acid and at high temperatures such a resin readily forms compounds which do not pass into a soluble state, diminish the yield of tannins, and lower the quality of the product.

The relative proportions of aldehyde and phenol effect the quantity of free phenol in the resin and the mean molecular weight of the oligomer. Subsequent sulphonation imposes no special restrictions on the degree of condensation. Up to 0.8 mole of aldehyde per mole of phenol, stable solubility of the product is reached even with small amounts of sulphuric acid. With regard to the relation between the extent of condensation and tanning ability, it was found that, contrary to expectation, no appreciable change in tanning properties was observed from the stoichiometric proportion and above. The optimum ratio can be regarded as 0.6 mole of aldehyde per mole of phenol. The condensation product is a mixture of molecules containing different numbers of rings linked through methylene groups. Analysis indicates that, with the above reactant ratio, the free phenol content is 15%, while the mean molecular weight of the polymer is about 500.

2. SULPHONATION OF PHENOLIC RESIN

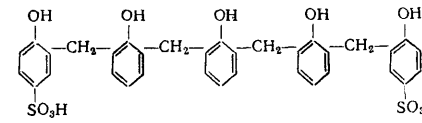
Sulphonation is the stage in the synthesis which determines the principal tanning parameters of the product. The same phenolic resin can yield tanning agents differing in forming and filling power from the lightest to complete substitutes, merely by variation in the proportion of acid to the resin. As this ratio is decreased, it becomes more difficult to obtain a product having stable solubility: it is necessary first to lower the moisture content of the resin, increase the acid concentration, raise the temperature, and prolong the process.

After separation from water the phenolic resin contains 15–20% of moisture. It is easily sulphonated by concentrated sulphuric acid in close to stoichiometric proportions (1.0 mole of monohydrate per mole of phenol), as is required in the preparation of light syntans. For heavy syntans the amount of acid should be halved, and here it is necessary to lower the moisture content in the resin to 3–4%. With further decrease in the proportion of acid, dissolution is achieved only by using oleum.

The results obtained on the relation between the tanning action of the product and the ratio of the reactants in sulphonation of the resin are given in Table 2.[35]

When small amounts of acid are used for sulphonation, a large proportion of it undergoes reaction. Thus with 0.5 mole of acid on the phenol, not more than 10% of the acid taken remains free in the sulphonated mass [43]. Calculation indicates that in this case the equivalent weight of the sulphonic acid is ~300.

With the molecular weight indicated above for a polymer of a normal phenolic resin ($M = 500$), the molecule of the tanning agent comprises on the average five phenolic rings associated with two or three sulpho-groups:



3. SECONDARY CONDENSATION

A feature of the entire series of tanning agents obtained by sulphonating a phenolic resin is their slow penetration into the leather in comparison with tanning agents obtained by the first alternative, i.e. products formed by the condensation of hydroxybenzenesulphonic acids. However, with the first few members of the series having a high proportion of sulphuric acid to resin this retardation is slight. As the quantity of acid decreases, the tendency of the tanning agent solutions to coagulate increases, and penetration into the leather becomes increasingly difficult, entailing very serious difficulties in practical application.

Table 2.

Molar ratio of acid (monohydrate) to phenol	Quality (ratio of adsorbable to dry substance)	Vol. yield of leather	Tanning coeff. of leather
0.9	49.5	220	34
0.5	65.9	301	56
0.4	79.0	322	60
0.3	84.6	378	87

This defect could be overcome by introducing an additional condensation of the sulphonated mass with small amounts of formaldehyde [44], which was carried out, after preliminary dilution of the sulphonated mass with water, at a low temperature (not above 50°C). Raising the temperature results in the appearance of insolubles, or even in complete insolubility of the product. A second condensation enhances the stability of the solutions, increases the content of tanning agents, considerably accelerates penetration into the leather, and improves its colour because dark, resinified particles are not now retained on the surface, but penetrate inside the leather. Thus a secondary condensation provides a very important method for all modifications of the given series of tanning agents, while for the heavier agents (in practice the most valuable) this can be regarded as essential.

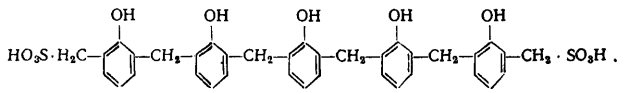
The course of the process depends to a considerable extent on the reaction of the medium. A decrease in acidity (partial or complete neutralisation of the sulphonated mass) lowers the reaction velocity, and condensation can be effected without complication at temperatures up to 75°C.[45] The quantity of aldehyde introduced in the second condensation has a fundamental effect on the properties of the tanning agent. It was established that, as the quantity of formaldehyde increased, the tanning properties passed through an optimum, after which they deteriorated considerably. With a normal resin (see above) this optimum occurs at a molar ratio of formaldehyde to phenol of ~0.1 : 1.0.

The presence of a maximum on the curve for the variation in the tanning properties of phenolic syntans as the quantity of formaldehyde is increased applies only to condensation after sulphonation. Such a maximum is not observed with preliminary condensation. Consequently this finding cannot be attributed to the increase in size of the molecule. It must probably be ascribed to the introduction of hydroxymethyl groups into the phenolic rings, which takes place under the mild conditions of the secondary condensation. In small quantities hydroxymethyl groups may have a favourable effect, by enhancing the hydrophilic character of the product and promoting the penetration of enlarged particles of the tanning agent into the fibrillar structure of the leather. However, the intensification of this property leads to a diminution in bonding and affects the occurrence of osmotic processes linked with the formation of the structure of leather.

4. SULPHOMETHYLATION OF PHENOL

With formaldehyde and sodium sulphite phenol undergoes two simultaneous reactions—the usual condensation with an aldehyde and sulphomethylation or introduction of a $CH_2.SO_3H$ group into the phenolic ring—the degree of condensation and the extent of sulphomethylation (mean equivalent weight of the sulphonic acid) depending on the proportions of the reactants and also on the process conditions. The best results with respect to product quality and reproducibility are obtained when the process is conducted in stages. The first stage—preliminary condensation of phenol with formaldehyde—is conducted under the same conditions—in acid medium with 0.5—0.6 mole of aldehyde based on the phenol—as for the sulphonic acid type of tanning agent. The second stage (sulphomethylation) requires, according to the equation for the reaction, equimolecular quantities of formaldehyde and sulphite; thus the proportion of sulphite based on the phenolic resin predetermines the proportion of formaldehyde. The sulphite : phenol ratio, however, can be varied within wide limits. Depending on this the tanning properties of this type of syntans also vary, just as those of the condensed hydroxybenzenesulphonic acids vary with the acid : phenol ratio adopted in sulphonating the resin.

By decreasing the proportion of sulphite to the initial phenol in the resin it is possible to obtain a series of tanning agents (FB) having enhanced tanning power like the FT series, obtained by sulphonating a phenolic resin. The molecule of the FB tanning agent from a normal resin with a molar ratio of sulphite to phenol of 0.5 : 1.0 contains on the average two sulphomethyl groups associated with five phenolic rings:



This product is a complete substitute syntan.

During sulphomethylation part of the aldehyde is consumed in further condensation with the phenolic resin, so that the sulphite does not enter completely into the condensation. With small amounts of sulphite this may result in inadequate solubility of the product, to prevent which it is advisable to increase the proportion of formaldehyde, i.e. to add rather more than an equimolecular quantity relative to the sulphite. Use of an increased proportion of aldehyde gives a soluble product even with 0.25 mole of sodium sulphite based on the initial phenol. As with an additional concentration after sulphonation of the resin, the variation in tanning properties with increasing amount of formaldehyde passes through an optimum here.

Compared with the analogous tanning agents of the FT series, the FB syntans, obtained by sulphomethylation of a phenolic resin, are distinguished by improved filling power and are less sensitive to changes in the active acidity of the solutions [35].

5. DISPERSION OF PHENOLIC RESIN IN SULPHONIC ACIDS

A phenolic resin is brought into colloidal solution by prolonged stirring with a solution of a sulphonic acid at

80–100°C. The process is favoured by high solute concentrations. Dilution considerably lengthens the process and diminishes the amount of resin which can be dispersed.

Before addition of the phenolic resin the sulphonic acids should be brought to their normal tanning power by condensation with aldehyde. Dispersion of the resin in uncondensed naphthalene- or hydroxybenzene-sulphonic acid gives a tanning agent of poor quality, which cannot be substantially improved by subsequent condensation of the dispersed product with formaldehyde.

Sulphonic acids exhibit active dispersing power only in the free state. Salts of sulphonic acids do not possess this ability, even in concentrated solutions, but sulphonic acids which have undergone normal improvement with a phenolic resin can, in the concentrated state or in solutions, be neutralised or subjected to other chemical treatments without breakdown of the colloidal system.

As has already been stated, the quantity of resin which can be introduced into the sulphonic acid depends on the solute concentration. Therefore the preliminary condensation of sulphonic acids with a considerable volume of formalin is an unfavourable factor in this respect. Modified processes in which preliminary condensation is not required, or is limited to a small quantity of aldehyde, permit greater improvement (e.g. the sulphonic acids from crude anthracene). The dispersing power depends also on the nature of the acid. In this respect sulphonic acids of tricyclic hydrocarbons are superior to those of bicyclic hydrocarbons. But ligninsulphonic acids (sulphite liquors) are especially active dispersing agents for phenolic resins: even in the neutralised state at a concentration not exceeding 50% they can bring up to 30% of the resin (based on the dry substance) into colloidal solution.

The tanning properties of the products obtained by dispersing a phenolic resin in any sulphonic acid are improved by further condensation with small amounts of formaldehyde.

6. ADJUSTMENT TO NORMAL ACIDITY

The final stage is adjustment of the acidity of the tanning agent to that required for practical application. Products of sulphonation of the resin or its dispersion in aromatic sulphonic acids require to be neutralised, which is accomplished with sodium carbonate or ammonia to a slightly acid reaction. Sulphomethylation produces a considerable quantity of alkali, and the product must be acidified with sulphuric acid. Dispersion of a phenolic resin in concentrates of sulphite liquors takes place in weakly acid medium, and these tanning agents do not require adjustment.

The shortage of phenol during the postwar period made it necessary to use more readily available starting materials—technical mixtures of phenols which could be extracted from tar waters formed in the thermal processing of bituminous shales and in the low-temperature carbonisation of coal. Work on these lines was conducted in the Central Scientific Research Institute for the Leather Industry by Konovalenko, Khadyk, Kuraitis, Golubeva, and Filippova.

By means of procedures developed previously (condensation with formaldehyde and subsequent sulphomethylation or dispersion in sulphonic acids) it proved possible to obtain from the extractable phenols a series of brands of substitute syntans, which found wide practical application under the designations No. 5, No. 12, SL, and SPS [46-48].

The most interesting of these tanning agents is SPS, obtained by the method proposed by Konovalenko [49]. The extractable shale phenols (mainly homologues of resorcinol) are condensed by this method with ligninsulphonic acids and formaldehyde, and the condensation product is dispersed in the spent liquor from the fermentation of sulphite-cellulose liquors to alcohol. From its tanning power SPS cannot be regarded as a full substitute, but it confers a light natural colour on leather and is readily compatible with other types of tanning agents.

Syntans obtained by the sulphomethylation of a polyphenolic resin possess substantial disadvantages—the dark colour and unpleasant odour which they confer on the leather, and also the inadequate standardisation of the product due to the variability in composition of the raw material—which suggests that such brands will not be kept in the range, and in the very near future will be replaced by syntans based on crystalline phenol. The production of brands from pure phenol by the methods described above has been growing rapidly during recent years. Among them are No. 2 [50] (an analogue of ST-50, differing from the latter in the use of ammonia for neutralisation), No. 3 (identical with LF), and FB-2 [51] (a modified form of FB, in which phenol has been replaced by the phenolic fraction of coal-tar).

C. Methods of Producing Substitute Syntans Abroad

At the end of the war information was published on German materials [52] and also literature surveys [17] on the production of German brands of synthetic tanning agents, so that it became possible to compare the development of ideas and practical methods for obtaining substitute syntans in the USSR and in Germany.

It turned out that the features which were mentioned in the pre-war foreign literature (see above) were secondary criteria. The German Tannigans extra did not belong to any new chemical types, but were the same sulphonic acids improved with phenols or their derivatives. Thus the general direction of German and Soviet work in producing substitute syntans was the same, but the initial attitudes and the methods by which improvement was accomplished were fundamentally different. The same task—to enlarge the particle size and increase the phenolic loading on the sulpho-group—was understood differently by the German chemists and by ourselves. Soviet investigators started from the observed possibility of dispersing the phenolic resin, and saw a solution to the problem in obtaining a coarse colloidal particle by intermolecular interaction between the phenolic oligomer and condensed sulphonic acids. German chemists thought it necessary to increase the size of the tanning agent molecule, i.e. to combine phenolic and sulphonic-acid components chemically by condensing them simultaneously with aldehydes ("mixed" condensation) [53].

In spite of the fundamental difference, these methods yield products which are analogous chemically and exhibit similar behaviour towards leather. As a consequence of this there is a considerable affinity between the German Tannigans extra and the same types of Soviet brands of heavy syntans.

It should be remarked that mixed condensation is a more complicated procedure than dispersion. It breaks down into several individual condensation of the initial compounds in various combinations, and results in the formation of a mixture of substances differing in chemical composition and structure, whereas with dispersion the final

result is determined unambiguously by the relative proportions of the components. In virtue of this, colloidal improvement creates more favourable conditions for studying theoretical aspects of the interrelation between the structure and the tanning properties of synthetic tanning agents. This may well be the reason why the researches aimed at producing the Soviet substitute syntans led to broader generalisations than did the foreign work. Among such generalisations are—(*a*) the absence of a direct connection between the chemical class of a tanning agent and its properties in relation to leather, (*b*) the concept of the chemical type of tanning agent as a kind of "homologous series" with a gradual change in tanning power, (*c*) the difference in the ratio between the parameters of forming and filling power for different chemical types ("homologous series" of tanning agents), and (*d*) the possibility of a rational specification of syntans from the point of view of leather technology, based on the ratio of the parameters representing forming and filling power [54].

Examination of prewar German methods for obtaining substitute syntans and their comparison with postwar methods described in foreign patents show that the principles laid down in this field in the 1930s have been fully maintained. A few new specialised brands of synthetic tanning agents have appeared since the war, but nothing fundamentally novel has been introduced into the methods of synthesising the substitutes. The present-day range of substitute syntans abroad comprises brands belonging to the same chemical types as were developed in Germany and in the USSR during the prewar period.

1. IMPROVED SULPHONIC ACIDS OF AROMATIC HYDROCARBONS

Tanning agents of this type are obtained by linking aromatic sulphonic acids with phenolic rings through a methylene group. This can be accomplished by the simultaneous condensation of sulphonic acids and phenols with formaldehyde, or by the condensation of sulphonic aicds with phenolic alcohols or resol resins [55]. Methods have been described also for linking through sulphur (condensation with sulphur monochloride) or through the sulphonyl group heating naphthalenesulphonic acids with hydroxybenzenesulphonic acids to a high temperature, when sulphonic acids of mixed hydroxyphenyl naphthyl sulphones are formed) [56]. Naphthalene- or benzylnaphthalene-sulphonic acid is used as the acid component, and ordinary phenol, tricresol, a polyhydric phenol, or bishydroxyphenyl sulphone as the phenolic component.

The simultaneous condensation of hydrocarbons with phenols is made difficult by the marked difference in their reactivity towards formaldehyde. As a consequence, the condensation products are very inhomogenous in composition, and contain a considerable quantity of insoluble compounds dispersed in the sulphonic acids.

Tanning agents of this type are not above the average in forming and filling power, and they cannot be regarded as complete substitutes. Rather they must be included in an intermediate group of syntans, destined for the manufacture of light types of leather or for combination with vegetable extracts in relatively small proportions.

The best product of this type is that resulting from the mixed condensation of naphthalenesulphonic acids with bishydroxyphenyl sulphone. With a high sulphone : naphthalene ratio it reaches the level of complete substitutes in its tanning action [27].

2. IMPROVED HYDROXYBENZENESULPHONIC ACIDS

This is the most widely represented type of tanning agents, and several methods have been proposed for obtaining them—mixed condensation of hydroxybenzenesulphonic acids with phenols and aldehyde, condensation of hydroxybenzenesulphonic acids with phenolic alcohols, etc.

Phenol, tricresol, the naphthols, mono-, and dihydroxybiphenyls, polyhydric phenols, and bishydroxyphenyl and bishydroxytolyl sulphones have been used as the initial compounds containing phenolic hydroxyls. Besides the usual mixing of the components, mixtures of them are sometimes obtained from the same starting material by an incomplete intermediate process. For example, a mixture of hydroxybenzenesulphonic acid and bishydroxyphenyl sulphone is obtained from phenol by heating it to a high temperature with a quantity of sulphuric acid insufficient for sulphonation [57]. The preliminary or mixed condensation of hydroxybenzenesulphonic acids with formaldehyde and phenols is often carried out with the addition of urea, which improves the colour of the leather [58].

The most valuable variant in practice is sulphonation of a Novolak phenolic resin until it is completely soluble, followed by condensation with formaldehyde [59]. The tanning agent "extra B" obtained in this way is very similar in tanning properties to our FT-50. [60]

Tanning agents of this type are characterised by a predominance of forming over filling ability. Their chief purpose, therefore, is the tanning of Russia leather, as well as of the less durable types of leather for the base of footwear and for technical uses.

3. PRODUCTS OF THE SULPHOMETHYLATION (ω-SULPHONATION) OF PHENOLS

Sulphomethylation is one of the processes generally used to obtain substitute syntans, and is employed in various ways. The starting materials used are phenol and its homologues, polyhydric phenols, dihydroxybiphenyl, bishydroxyphenyl sulphone, or products of their preliminary condensation with formaldehyde in acid or alkaline medium. In foreign practice, however, this process is probably used predominantly to obtain tanning agents of mixed types. By itself the ω-sulphonic-acid type is of secondary practical value. This can be explained by the lower solvent power of such sulphonic acids for vegetable extracts in comparison with the usual hydroxybenzenesulphonic acids.

Independent application is found mainly with products of the sulphomethylation of bishydroxyphenyl sulphones [61].

4. LIGNINSULPHONIC ACIDS IMPROVED WITH PHENOLS

A feature of substitute syntans obtained by improving ligninsulphonic acids is their good filling power and the enhanced durability conferred on the leather, which makes them especially valuable for the manufacture of sole leather. With respect to the place they occupy in the foreign range, tanning agents of this type are as important as improved hyroxybenzenesulphonic acids.

The starting material for their production consists of the waste lyes from the manufacture of sulphite cellulose or the spent liquor remaining after their fermentation into alcohol. These liquids are usually freed from calcium salts; sometimes they are subjected to other forms of preliminary treatment, e.g. heating with alkalis under pressure to diminish the quantity of combined sulphurous acid.

A general method of improvement is the mixed condensation of sulphite concentrates with phenols or their derivatives in acid or alkaline medium[62]. The chief brand of this type, which has remained in the German range for thirty years, is a product of condensation with bishydroxyphenyl sulphone ("extra A"), which is similar to our LF in tanning properties[60].

Various ways of using mixed condensation to improve ligninsulphonic acids are given in patents. Conducting the process in two stages is of practical value: (*a*) preliminary condensation of a phenol or a sulphone with formaldehyde is followed by mixed condensation of the product with the sulphite liquor; (*b*) mixed condensation of the liquor with a phenol or a sulphone yields a product which is separated from the solution, and dispersed in a fresh portion of liquor. Ligninsulphonic acids improved with phenols are easily salted-out from solution by electrolytes. This enables a tanning agent of this type to be obtained as a solid product having a high content of tanning agent[63].

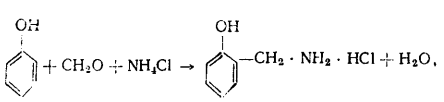
Together with tanning agents belonging to the individual chemical types described above, the foreign range contains a large number of brands of mixed types, i.e. obtained by combining two or more modes of improvement, or representing simply mixtures of ready made tanning agents of different types. For example, phenol (cresol) is condensed with a mixture of hydroxybenzene- and naphthalene-sulphonic acids[64]; phenol or bishydroxyphenol sulphone is condensed with a mixture of ligninsulphonic and aromatic sulphonic acids[65]; hydroxybenzene- or hydroxynaphthalene-sulphonic acids, after being condensed simultaneously with phenol and an aldehyde, are mixed with ligninsulphonic acids which have previously been improved by condensation with phenol and formaldehyde[66]; a product of the sulphomethylation of bishydroxyphenyl sulphone is subjected to mixed condensation with hydroxytoluenesulphonic acid, bishydroxyphenylpropane, and formaldehyde; etc.[67]

A noteworthy feature of the numerous variants of this kind encountered in patents of the war and postwar periods is that they reflect no tendency at all to further specialisation of the tanning agents in relation to leather technology, in particular any strengthening of the characteristics of substitute syntans. On the contrary, these modifications are directed to obtaining tanning agents of intermediate type as regards leather technology, in which the forming and filling ability is controlled at the level necessary for the solution of additional problems not directly connected with the replacement of vegetable extracts.

IV. NEW TYPES OF SYNTHETIC TANNING AGENTS

1. Amphoteric Tanning Agents

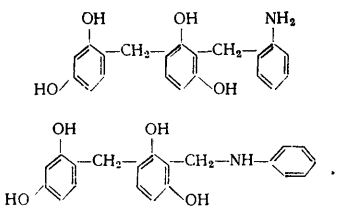
Up to the end of the 1940s all methods for obtaining synthetic tanning agents, whether operated industrially or only described in the literature, yielded products in which the tanning action was located in an anion. At the beginning of the past decade tanning agents of a new chemical type, have a tanning cation, appeared in the Federal Republic of Germany. Their mode of production, developed by Mauthe and Farber[68], consisted in the simultaneous condensation of an ammonium or an amine salt with a phenol and an aldehyde:



Compounds of this type dissolve readily in acid medium as substituted ammonium salts, and in alkaline medium as phenoxides. The tannophoric groups—phenolic hydroxyls—are located in the former case in the cation, and in the latter case in the anion. This gave rise to the name amphoteric synthetic tanning agents[69,70] which is really incorrect, since they exhibit tanning activity only in acid medium. In contrast to the usual synthetic tanning agents, the tanning power of amphoteric syntans (their combination with a protein) increases as the acidity diminishes. At the isoelectric point they are precipitated from solution. A characteristic property of the new tanning agents is the formation with anionic compounds—tanning agents, dyes, fat-liquoring sulphonated products—of insoluble salts: this property permits their use both as tanning agents and as fixing agents, anchoring the anionic products in the leather. This second use, which requires only a relatively small amount of the syntan, is of far greater practical interest than is the first. However, the simultaneous tanning action gives a substantial additional effect, which is a valuable distinguishing feature from other types of fixing agents.

The tanning action of amphoteric syntans depends on the nature of the initial compounds and on their relative proportions. In this respect these agents resemble anionic syntans. The tanning power of sulphonic acids improved with phenols increases with increase in the phenolic loading on the sulpho-group; in amphoteric tanning agents the phenolic loading on the amino-group has an analogous effect: as the amount of phenol combined with the amine increases, the tanning agent approaches closer and closer to the heavy type.

Products obtained by the Mannich reaction from phenols possess very weak tanning action, since they achieve stable solubility only at a high amine : phenol ratio. Products whose tanning action is comparable with that of substitutes can be obtained only by the simultaneous condensation of a polyhydric phenol with formaldehyde and an aromatic amine, e.g. by the condensation of resorcinol with formaldehyde and aniline with a molar amine : phenol ratio not exceeding 0.5 : 1.0. In this case the reaction can go in two ways, with formation of the compounds:



The condensation leads predominantly to a product of the type (I).

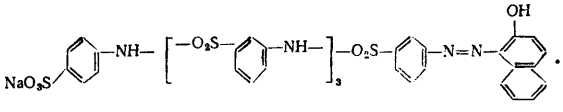
Methods were developed for obtaining amphoteric tanning agents based on technical mixtures of polyhydric phenols from tar water from the low-temperature carbonisation of coal. In the first modification the process is conducted in stages, the amine being introduced into the reaction in two portions with intermediate cooling[71]. This makes solubility easier to achieve, and enables mixtures of polyhydric and monohydric phenols to be used. In a second modification formaldehyde is replaced by bishydroxymethylurea[72], which lowers the heat of reaction and facilitates its occurrence.

When tried on an industrial scale the amphoteric tanning agent LAF, which we have obtained, exhibited a high tanning power.

2. Dyes with Tanning Ability

Acid and direct dyes exhibit some structural similarity to synthetic tanning agents. This explains their tanning ability, which is developed to different extents depending on the molecular weight and structural features[73]. In the usual dyeing of leather, in spite of the small consumption of dye, the tanning action of certain dyes has an appreciable effect on the physical properties of the surface layer. In comparison with syntans, of course, the tanning power of dyes is small, not surpassing the lower grades of the auxiliary type. However, it could be considerably strengthened by increasing the organic loading on the sulpho-group and introducing tannophoric groups into the molecule, provided that the chromophoric system is not disturbed.

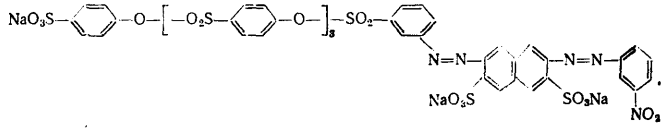
Dyes of this type were first prepared by Berkman and Gordinskii[74]. They were azo-dyes in which the diazo-component contained a polycyclic polysulphonamide chain as is usual for synthetic tanning agents of the polysulphonamide type[75,76]:



Further studies have been made of the synthesis and properties of polysulphonamide azo-dyes[77,78]. Analogous compounds were obtained containing sulphonamide groups in the coupling component, and symmetrical and unsymmetrical *cis*- and polyazo-dyes containing chromophores isolated by a polycyclic polysulphonamide chain.

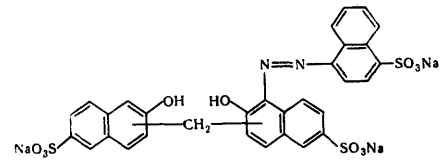
All these dyes exhibited high tanning power, evenness of coloration, and fastness to wet rubbing. The increase in levelling power is interesting, for this usually becomes worse with increase in size of the dye molecule. In the present case the colour is probably influenced favourably by the simultaneous differentiation of the fibre structure of the outer layer of the leather, which contributes to a uniform distribution of the dye.

Azo-dyes having similar properties are obtained[79] by introducing a polyaryloxysulphonyl chain or a mixed chain containing sulphonic ester and sulphonamide groups into the molecule[80,81]:



Polysulphonamide and poly(sulphonic ester) dyes are individual compounds, and can be obtained as crystals. By varying the length of the chain it is possible to obtain for each dye a series of compounds containing the same chromophoric system but differing in number of tannophoric groups and in molecular weight. This makes it possible to study certain aspects of the relation between the molecular structure and the physicochemical and dyeing properties of dyes[75,77,78,81].

Dyes which already contain tannophoric groups (phenolic hydroxyls), but exhibit only slight tanning activity, can be made active tanning agents by enlarging the molecule. This is accomplished by condensing the base or the coupling component with an aldehyde or a ketone, as in the analogous condensation of sulphonic acids in the preparation of synthetic tanning agents. Various dyes of this type, e.g.



have been prepared[82], and found to possess high forming and filling power.

An analogous method was suggested at the same time in the German Democratic Republic for the preparation of tanning agents possessing dyeing properties by coupling ordinary diazo-components with phenolic syntans of various types[83].

Dyes exhibiting tanning properties may be of considerable interest in the production of leather for shoe uppers and especially for special types of leather—fancy, garment, glove leathers.

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The production of synthetic tanning agents is at the present time an established branch of fine organic synthesis with a wide range of products intended to replace vegetable tanning extracts and for several purposes of ancillary or special character. The development of this industry in individual countries is determined by the economic conditions, which differ fundamentally.

On the world market vegetable tanning materials, imported predominantly from former colonies or semi-colonial territores, are considerably cheaper than artificial tanning agents. In capitalist countries (especially England and the USA), therefore, the use of substitute syntans on a large scale is not yet justified. Practical interest attaches mainly to their application for special purposes.

The position in the USSR is completely different. Although we have fairly large potential resources of raw materials for the production of tanning extracts, the raw material itself is characterised by a low content of tannins, and is mostly situated in remote, relatively undeveloped regions. Its procurement and transport involve great organisational difficulties and great expense. In the USSR, therefore, vegetable tanning agents are almost twice as dear as the synthetic products. In this situation our most important task is to use syntans to replace vegetable extracts in as large a volume as possible. With an annual demand by the leather industry for ~ 150 000 tons of dry tanning extracts, this provides grounds for developing the manufacture of syntans to the level of a large-scale and economically very efficient branch of the chemical industry.

The possible applications of artificial tanning agents are not restricted to the leather industry. In their structure and physicochemical characteristics these substances are water-soluble polymers, and may find various uses as a special group of such substances. Recent developments in the synthesis of products which combine tanning action with other functions—fixing, dyeing, emulsifying—open up for synthetic tanning agents new prospects of theoretical and practical interest.

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