Degradation by Ultra-violet Light of Wool and other Textile Fibres.

by

Roshan Lal Shishoo

ABSTRACT

Physical and chemical changes occuring in wool as a result of exposure to ultra-violet light have been investigated. The methods used included the determination of strength, extensibility and reduction in work of rupture, the measurement of density, refractive index, urea-bisulphite solubility, alkali solubility, water imbibition, specific surface area, dye absorption and X-ray diffraction.

There is a progressive decrease in strength and extensibility and hence an increase in the reduction in the work of rupture of the wool fibre after successive doses of ultra-violet radiation. Increases in density and refractive indices of the wool fibre were observed, which indicated an increase in crystalline - amorphous ratio, probably due to molecular chain readjustment effected by ultra-violet energy. The imbibition value and the specific surface area of exposed wool fibres was reduced, showing that accessibility to certain reagents was lowered after exposure or that the structure became more compact in the molecular sense. No appreciable changes in X-ray

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photograph were however observed to confirm these effects.

That the exposure of wool resulted in degradation of main-chains and disulphide linkages was shown by the increase in urea-bisulphite solubility and alkali solubility after irradiation. The rate of dye uptake of wool fibres was enhanced after exposure. The dyeing rates of unexposed and exposed descaled wool were apparently equal. One of the main effects of irradiation on intact wool was therefore modification of the cuticle.

The examination of degradation by ultra-violet light was extended to other fibres. Losses in strength, extensibility and reduction in work after exposure were recorded for matt and bright M 95, viscose rayon, Acrilan, Matt Courtelle, Fibrolane BX and nylon 66. The light stability of acrylonitrile fibres seems to be very good, followed by nylon, viscose and Fibrolane BX in that order. The results of strength tests showed that the presence of a delustring agent increased the degree of fibre degradation. Ultra-violet exposure resulted in an increas in fluidity of viscose rayon, and a diminution of the viscosity and molecular weight of nylon. This suggests that in both viscose rayon and nylon,rupture of the main chain molecules has occured.

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DEGRADATION BY ULTRA-VIOLET LIGHT OF WOOL AND OTHER TEXTILE FIBRES

A THESIS

submitted

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SUMMARY

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INTRODUCTION

1.01 - PHOTOCHEMICAL DEGRADATION OF TEXTILES

It is well known that the prolonged exposure of textile fibres to light can result in photochemical degradation, one of the best known illustrations of this being the difference in properties between the protected portion and exposed tip of a wool fibre.

In order to produce a photochemical change in any material, light must not only be absorbed, but also be of sufficiently high energy content to excite the molecules of the irradiated substance resulting in their chemical reaction or dissociation. Two essential features of the molecules of which the textile fibres are composed, the length of the molecular chain and the cohesion between adjacent chains, may be affected by these changes.

Atoms and molecules emit or absorb radiation only in discrete energy steps known as quanta, the magnitude of a quantum being directly proportional to the molecular frequency of a substance, each molecule taking up one quantum of radiation in acquiring its activated state. A molecule can acquire more energy from a high frequency radiation than from radiation of a low frequency. Table I gives some values for the wavelength, frequency and quantum energy of radiation in a particular range of the spectrum.[1]

TABLE I

Range of the Spectrum	Wavelength Å	Frequency $10^{14}sec^{-1}$	Energy per quantum 12^{-12} ergs
Near infra-red	10,000	3.0	2.0
Visible (red)	7,000	4.3	2.8
Visible (green)	5,500	5.5	3.6
Visible (violet)	4,000	7.5	5.0
Near ultra-violet	3,500	8.6	5.7
Far ultra-violet	2,500	12.0	8.0

It will be seen that radiation in the near ultra-violet can provide about three times the energy per quantum of that in the near infra-red region. The fundamental laws of photochemistry show that the absorption of radiant energy will produce chemical changes to an extent dependant upon the frequency of radiation, higher frequency radiation producing the greatest changes.

As received at the surface of the earth, the solar radiation spectrum may be divided[2] approximately as shown in Table II

TABLE II

	Range Å	Percentage of total radiation
Ultra-violet radiation	2000-3800	4
Visible radiation	3800-7600	43
Infra-red radiation	above 7600	53

Although only four per-cent ultra-violet radiation is received by the material from the solar radiation, the changes produced within the fibre are appreciable compared with those produced by the remaining 96 per-cent radiation. Thus, although sunlight is in practice the medium responsible for light degradation of textile materials, in order to investigate the effect of shorter wavelength (high frequency) radiation, an ultra-violet light source has been used. This has the advantage of consistency of intensity, whereas the intensity of daylight is a variable factor. Ultra-violet radiation has the experimental advantage of producing measurable degradation within a reasonable period of time.

The xenon arc has been found[3] to give the best approximation to sunlight, particularly for the ultra-violet and for shorter wavelength ultra-violet (below 3500 Å), while the combination of fluorescent Sunlamp and Blacklight lamp also approximates to sunlight. Elliot et al[4] used Davis and Gibson liquid filters and a tungsten lamp to provide a light source for which the spectral energy distribution approximated to that of the sun. Appleby[5] found that of the available light sources, the high intensity carbon arc with appropriate filters appeared to give the most reproducible results.

An unavoidable factor, when an ultra-violet source is used, is that ozone is produced by the radiation which might directly, or indirectly, affect the degree of degradation caused by the ultra-violet radiation. However normally ozone is not an important factor in wool degradation since the ozone-producing radiations of wavelength 1850 Å are absorbed by I mm of air at atmospheric pressure.

In the action of light on textile materials there are two main types of photochemical action of importance namely, photolysis and photosensitisation[6].

1.02 - Photolysis

In this type of reaction, the radiation absorbed by a molecule produces disruption of a chemical bond with consequent loss of strength of the textile fibre. The rupture of the chain molecules involves breaking single bonds of either carbon-carbon, carbon-oxygen, or carbon-nitrogen depending on the fibre, while changes in side linkages may involve carbon-hydrogen in addition. The energy required to produce these molecular disruptions is relatively high; in fact it is only the radiation at the shorter wavelength end of the ultra-violet spectrum (wavelength in the 2500 Å region) which has sufficient energy per quantum to promote these reactions. These photolytic effects are a direct result of irradiation and do not depend on the presence of oxygen in contact with the irradiated material, while they also occur when the textile fibre is exposed in an inert atmosphere or in a vacuum.[7] In the photolysis of all macromolecules, the energy required to produce a cleavage in a chemical bond will depend on the nature of the bond and the atoms involved.

1.03 - Photosensitisation

In some systems where the reactant is incapable of absorbing the incident light to any considerable extent, for a chemical change to occur it is necessary to introduce into the system a substance capable of absorbing the light and of conveying the energy so absorbed to the reacting molecules. When this energy is sufficient to cause reaction, and provided that the absorbing substance is not permanently transformed thereby, the process is known as Photosensitisation The presence of oxygen is essential, the rate of reaction being neglegible in its absence as has been shown where irradiation of dyed and undyed fibres in vacuum, or in the presence of inert gases, did not result in significant degradation.[8-11] This type of reaction can be initiated in both near ultra-violet, or visible, regions of the spectrum depending on the type of sample. Moisture is another environmental factor which, with many types of material, can effect a very great increase in the magnitude of photochemical change. When a radiation-absorbing substance such as a dye or pigment is associated with a fibre, absorption of light or near ultra-violet radiation may be increased and the energy transferred to the reacting molecules of the fibre so as to initiate photo-oxidation. Such dyes or pigments are known as photo-sensitisers and many dyed textiles will consequently exhibit greatly enhanced degradation in light compared with the undyed material. Even colourless pigments such as zinc oxide and titanium dioxide, which have strong absorption in the near ultra-violet, will act in this way as photo-sensitisers.

A general scheme of the mechanism involved has been suggested,[10,11,12] in which the light energy absorbed by the dye is transferred to the oxygen in the surrounding atmosphere with the production of activated oxygen. In the presence of water vapoure, the activated oxygen is assumed to react with the formation of hydrogen peroxide. The degradation of the textile material is then due to oxidation by activated oxygen and/or hydrogen peroxide, depending on the particular textile fibre and the experimental conditions.

1.04 - Effect of Temperature

The extreme differences in atmospheric temperature between such situations as high level stations, cultivated fields, rocky outcrop (large), thick vegetation and deep water (small) and in free air above 4,000 ft. above the surface (zero), result in severe physical and chemical damage, the degradation being greater at places with higher temperature.[19]

1.05 - Effect of Humidity

Ashton and Probert[24] studied the photochemical degradation of dyed fabric by daylight under controlled humidity conditions in an attempt to find a relation between the relative humidity of the atmosphere and the extent of photochemical degradation of vat-dyed cotton. In general an increase in humidity usually increased the degradation, although the effect depended upon the nature of the fibre. Egerton[19] showed that the effect of atmospheric humidity on the rate of photochemical degradation was not great for bright nylon and bright viscose rayon yarns, but was considerable for the silk and cotton yarns, and very great for dull viscose rayon. The degradation of dyed and undyed cotton and silk is increased by moisture, and these textiles are markedly affected by the volatile peroxide. On the other hand the degradation of nylon and viscose rayon is much less affected by humidity, and the effect of the volatile peroxide on these fibres is much less than in cotton.

1.06 - Other Factors

The rate of degradation of a textile material is greatly influenced by the intensity of the radiation used and the time of exposure, and is increased by the increase of both these factors. Flynn[16] has shown that the number of fractures per chain in cellulose is proportional to the light intensity.

The physical structure of the material exposed is also of some importance when considering the possible degree of degradation. The coarser yarns are less susceptible to damage than the finer ones, while in the case of wool fibre it has been shown that substantial damage by ultra-violet light is caused to the scales which in turn may be regarded as giving protection to the cortex.

The order of severity of ultra-violet degradation changes with the fibres of difference chemical structure. Sippel[17] has classified the light stability of various fibres as shown in Table III.

TABLE III

Fibre	Light stability
Polyamides	little
Wool	little
Natural Silk	little
Cellulose Rayon	moderate
Cellulose Acetate	good
Acrylonitrile	very good
Polyvinylchloride	very good

1.07 - Physical and Chemical Effects

A progressive loss of strength and extensibility or "tendering" is probably the most important of the changes in the physical properties of fibres which follow photochemical attack. This provides a reasonable empirical basis of comparison that possesses considerable practical interest, and it has been used for this purpose.

The chemical or photochemical degradation of natural and man-made textile polymers is accompanied by change in the flow properties (fluidity, viscosity) of their solutions, and such a property might be chosen as a quantitative index of the extent of photochemical degradation. Unless such measurements could be reduced to somewhat more comparable forms, such as intrinsic viscosities, they provide no absolute basis for comparing the behaviour of different textiles, but they can be of comparative value in a study of the photochemical degradation of any particular fibre.

Having completed a general survey of the problem of photochemical degradation of textile fibres, certain fibres will now be considered individually.

1.08 - Wool

Harris and Smith[10] believed that ultra-violet light could disrupt the disulphide bonds of dry wool, so that eventually all the cystine was oxidised. The resulting degradation of wool, determined by alkali-solubility measurements, and by estimation of liberated ammonia and sulphate sulphur was directly related to the decrease in cystine content.[19] The primary action of radiation which resulted in the decomposition of cystine, was independent of the moisture in the system, and was believed to be a direct activation of the disulphide bond. This probably leads to the transient formation of ions, followed by hydrolysis (which was shown to be a photochemical process),[20] leading to the evolution of hydrogen sulphide from the unstable sulphenic acid, as given by:-

$$-\ CH-CH_2-S-S-CH_2-HC- \longrightarrow -CH-CH_2-S + S-CH_2-CH-$$

$$\downarrow H_2O$$

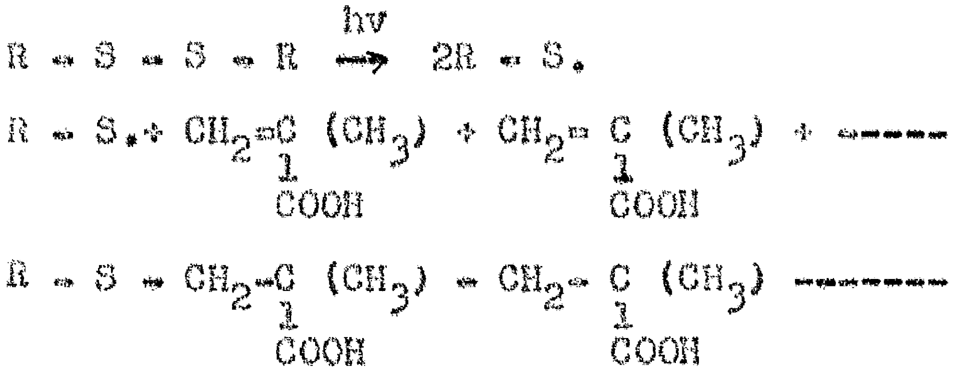
$$-CH-CH_2-SH + HOS-CH_2-CH-$$

The sulphenic acid ($HOS.CH_2-CH$) further decomposed to give hydrogen sulphide which was eventually oxidised to sulphate -

$$-CH-CH_2-SOH \longrightarrow -CH-CHO + H_2S$$

A direct cleavage of the disulphide bond of cystine itself by this type of reaction, has also been postulated by Anslow and Foster,[21] who showed that when radiant energy is absorbed by this substance, the linkages between the halves of the molecule were weakened, which resulted in the disruption of the molecule.

There is also evidence to show that free thiol radicals, R - S., can be formed by the dissociation of disulphides,[22] and further support for this was provided by the work done by Crawshaw and Speakman[23] in which the polymerisation of m-acrylic acid was promoted by cystine and ethyl disulphide. Since cysteine, lysine and iodogorgoic acid are without effect, there can be little doubt that the ability of intact wool to initiate polymerisation is due to the disulphide bond it contains. At 25°C, however cystine, ethyl disulphide and wool are ineffective in absence of light, and it was concluded that the free radicals which initiate polymerisation were formed by the fission of disulphide bonds under the influence of light.



$$R - S - S - R \xrightarrow{h\nu} 2R - S.$$

$$R - S. + CH_2{=}\underset{\substack{|\\ COOH}}{C}(CH_3) + CH_2{=}\underset{\substack{|\\ COOH}}{C}(CH_3) + \text{------}$$

$$R - S - CH_2 - \underset{\substack{|\\ COOH}}{C}(CH_3) - CH_2 - \underset{\substack{|\\ COOH}}{C}(CH_3) \text{--------}$$

The hydrolytic cleavage of the disulphide group of cystine in wool, by the action of light is similar to that postulated by Crowder and Harris[24] to account for the degradation of wool in alkaline solution.

Wool which is relatively more stable to light than silk,[25] is oxidized during irradiation, the chief point of attack being the disulphide group of the amino acid, cystine, which is present in wool but not in silk. The group is readily attacked by oxidising agents and becomes more susceptible to the action of alkalis.[26,27] The extent to which wool is oxidised bears a functional relationship to the decrease in its cystine content and to the increase in its alkali solubility. The total sulphur contents of the untreated and acid-treated samples decrease during exposure. Moreover hydrogen sulphide evolved readily oxidises to sulphuric acid, which would account for the comparative ease with which some of the disulphide sulphur in wool is converted to sulphate sulphur.[18]

The disulphide group absorbs ultra-violet radiation and although it was found that the amount of cystine lost in the irradiation was 25 percent of the total content, after exposure for 2 hours, no further increase in cystine loss was noticed up to 200 hours. On the other hand increase in exposure time from 2 to 20 hours greatly increased the supercontraction. It therefore seems unlikely that cystine takes any part in supercontraction process. Haly[28] et al suggested that tyrosine might be involved in the strong polar bonds or co-operative secondary bonds, which when broken in lithium bromide solution allowed the secondary supercontraction stage.

Barritt and King[29] found that the sulphur content of wool was reduced after irradiation and that it was still lower after washing with N/1000 sodium hydroxide. They considered the resultant loss of weight of wool was due to the detatchment of sorbed sulphur dioxide. That the extract must contain materials other than this was shown by the fact that it yielded a hygroscopic solid on evaporation, and that it absorbed in the ultra-violet region. The spectrum of the aqueous extract of irradiated wool is seen to resemble that of an extensively irradiated solution of tyrosine.[30,31] The aqueous extract spectrum is unaffected by a change in pH from 3 (the original) to 12. It is possible that oxidation of the phenolic component has taken place during irradiation, with the formation of dopa-quinone (3:4 - diketo phenylalanine) or similar residues which no longer contain ionizable groups. This oxidation mechanism is supported by the observation that heat-damaged (i.e., oxidized) wool gives a digest spectrum which indicates the production of a similar substance.

Differences in chemical composition between root, middle and tip sections of normal crimped, and of copper - deficient steely South African Merino wools were investigated by Louw,[32] as well as the influence of these differences on acid dye-absorption, alkali solubility and urea bisulphite solubility. In normal wools, the loss in cystine and tryptophan content and increase in cysteic acid revealed the extent of hydrolytic and oxidative weathering damage and explained the changes in solubility and dye absorption. Copper deficient root wools contain less cystine but more cysteine and cysteic acid, and have lower alkali solubility and dye-absorption than the normal wool, and were considered to be incompletely keratinized. Keratinization can continue as a result of an increase in cross-linking during ageing and weathering on the animal's back, thereby restoring the alkali-solubility and dye absorption to levels associated with normal weathered wools.

The tips of the wool fibres are known to have a low cystine content due to weathering, and it has been shown that cysteic acid is present.[33] As weathering involves the prolonged interaction of light and water with wool, the process which occurs should be similar to the photo-chemical reaction.

The alkali-solubility increases when wool is degraded either by peptide-bond breakdown or rupture of the disulphide bond and is a most useful method for assessing the damage. Moreover, disorientation of macromolecular structure resulting from the breaking of hydrogen bonds only (e.g., lithium bromide, phenol) also greatly increases the alkali - solubility although no covalent bonds have been broken.[10]

The absorption spectrum of the alkali solutions obtained during alkali-solubility tests of wool exposed to ultra-violet light, resembled that of wool which had been refluxed for 5 hours in 2N sodium hydroxide and both curves reproduced the characteristic minimum and maximum shown by tyrosine in 2N sodium hydroxide solution.[30]

The swelling in 0.1 N. sodium hydroxide is a function of the time of exposure to sunlight,[34] values of over 100 per cent resulting from exposing cloth for 600 hours (unexposed wool swells less than 10 per cent). This easy swelling makes exposed wool tips dye darker shades than the rest of the fibre in fast-to-milling acid dyes with large aggregated molecules, and lighter than the rest with some dispersed acid colours. The presence of -CHO and -SH groups inhibits the development of the full shade with some chrome dyes.[35]

That light has an important effect on the cuticle is shown by the fact that wool exposed in a Fade-O-meter is much more quickly wetted by a solution of a detergent, and by the reduction in shrinkage in washing and milling, after prolonged exposure. Moreover, an increased reaction is found with the Pauly test in which brown stains are formed with the tyrosine in the cortex.[36] (The cuticle is believed to have a few tyrosine residues).

Although exposed wool wets very readily, the amount of moisture which it contains when in equilibrium with an atmosphere of defined temperature and humidity, is rather less than with unexposed wool.[37]

According to Lundgren,[38] who attempted to explain the mechanism of yellowing of wool, the ultra-violet light energy is absorbed by the chromophoric groups, chiefly the aromatic and hetrocyclic centres and possibly the enolized peptide chain groups. It is known that the aclylation of hydroxy groups of tyrosine imparts a measure of protection to wool, silk and other proteins, indicating that phenolic groups are involved. However the fact that simple amino-acids such as alanine became yellow when treated with ultra-violet light led Lundgren to the conclusion that the yellowing mechanism is complex and that several processes may occur simultaneously. He found from the experiments with titanate esters that alkoxy radicals acting as free radical scavengers are the active agents effective for inhibiting the yellowing of wool by light. This yellowing can be inhibited by impregnating the wool with butyl phosphate and acetic anhydride, or better still with butyl titanate.

Graham and Statham[39] have attributed the yellowing of wool to the conversion of tryptophan into coloured derivatives and this claim was also confirmed by Lennox[40] who observed a fall in the content of tryptophan during irradiation.

Lennox[40] found that when wool was exposed for one hour to ultra-violet radiation with a 125 - watt lamp, a deep yellow shade was developed, the yellowing produced occuring slightly more readily in dry air than in moist air. Studies on yellowing were made by a differential spectraphotometric absorption method for measuring colour in wool.[41] The increase in absorption at 3200 Å which accompanies the disapperance of greenish colour developed under anhydrous conditions suggest that yellowing by ultra-violet irradiation can proceed by at least two steps. One of these is a photochemical step to give a green component which then reacts with water in a second step to give material with λ max at 3200 Å. The second step thereby intensifies the yellowing. A green-yellow shade is produced in dry wool fabric when exposed to ultra-violet irradiation over a desiccant, λ max occuring at about 6300 Å in addition to usual λ max at 3200 Å. On exposure to the moist air, the absorption peak at 6300 Å disappeared and the optical density at 3200 Å increased to a higher value than is obtained by radiation in moist air.

Amino acid analysis of wool fabric after yellowing and exposure of individual amino acids and peptides to irradiation treatment suggest that cystine was the amino acid chiefly responsible for the discolouration process. Castiglioni[42] suggested that the yellow colour produced when wool is exposed to ultra-violet radiation is due to the reaction of sulphuric acid, produced by the photochemical oxidation of cystine, with choloesterol and related compounds present in wool grease.

Bendit[49] measured the ultra-violet absorption spectrum of keratin, irradiated with ultra-violet light from a 125 W high pressure mercury lamp, and noticed an increase in absorption at wavelengths above 3000 Å. He suggested that the cause of the additional absorption is undoubtly associated with the yellowing of certain amino acids, particularly cystine, when exposed to ultra-violet radiation, but it might also be due, at least in part, to increased peptenolate absorption.[40]

Haly[41] found that the effects of radiation reach right into the near-axis region of the fibre and concluded that this might result from (i) diffusion of photochemical products (ii) more direct transfer of excitation energy by means of exciton diffusion or sensitised fluorescence.

Bradbury[45] has analysed cuticle - rich material and whole fibres from both untreated and irradiated wools, and concluded that the outer region of a fibre is no more affected by irradiation than the whole fibre.

It has been known for many years than one of the effects of ultra-violet radiation on wool is to increase the rate of uptake of some dyes. Other treatments which produce a similar result include modification of wool by alkali, by acid and by chlorination. Lindberg[46] concluded that reaction of alkali and acid with the fibre epicuticle was responsible for the increased rate of dye uptake in these cases. Haly[47] suggested that in case of ultra-violet irradiation of wool it is again modification of the epicuticle which is primarily responsible for the accelerated rate of dye uptake. Abraded pieces of wool fibres, irradiated and un-irradiated, were immersed in dye at room temperature on the same microscopic slide and examined at intervals for the depth of colour. Both irradiated and non-irradiated pieces appeared to dye at approximately the same rate, and were heavily dyed before an intact fibre on the same slide had achieved any appreciable colouration. It thus appears that if ultra-violet light affects rate of dye absorption by the wool fibre cortex the effect is secondary to modification of cuticle.

Haly[20] suggested that radiation had an important effect on tyrosine residues in wool, and Earland[40] supported the idea of a correlation between tyrosine modification and antifelting properties of wool, which might explain the difference in felting properties of wool after irradiation. He also found that the wool fibre, after ultra-violet irradiation from a high pressure mercury in quartz source, when heated in lithium bromide solution, supercontracted much more rapidly than normal fibres. These phenomena remain when wave-lengths shorter than 2900 Å are eliminated, but a longer time of irradiation is required. Rzegocinski and Lund[49] found that the damage caused by light was of similar type to that for alkali-treated fibres and the curves of supercontraction were also very much alike in shape. The modification due to light increases proportionately with the time of exposure. They have indicated the degree of such damage as "Recovery time" (RT) from the beginning of the reaction (taken as the time of immersion of fibres in the reagent) up to the point when the fibres have fully recovered in length from the supercontraction. This method of testing uses as a criterion of damage the time of recovery from supercontraction in ammoniacal caustic potash since this makes a clear distinction between different modification in the fibres caused by acid, by alkali, or by light.

Wools that have been weathered during growth felt more readily than less exposed wools,[90] though cloth that has been exposed to daylight for several weeks felts much less than unexposed fabric.[97]

McMohan and Speakman[91] have shown that slight tension during irradiation does not affect the degree of damage suffered by the fibre. From X-ray observations Astbury and Woods[92] stated that irradiation of unstretched keratin by ultra-violet or X-rays causes inter-molecular changes analogous to those due to the action of water on stretched keratin.

The work required to stretch a single wool fibre 30 per cent of its length in water at a standard temperature is characteristic of that fibre, and reproducible within 2 percent if the fibre is rested in water for 24 hours between extensions. If the cross-links in the keratin molecule have been attacked in any way, the work to stretch is affected, the change being a measure of the extent of damage.[59] Irradiation produces this effect, since disulphide cross-linkage groups are hydrolysed[18] and other changes also take place. Change in work of stretch is clearly of importance in manufacturing processes in which the elasticity of wool comes into play.

It has been shown that the primary process occuring in photochemical attack on wool fibre is the breakdown of the disulphide bonds with the formation of sulphydryl and aldehyde side chains, and that the changes in the physical characteristic of the material, changes in dyeing reaction, and the increased solubility of wool protein are all secondary developments. It is known that the reactions responsible for the production of permanent set, which occur on treating the stretched fibres under specific conditions, are dependent on the pre-existence of intact disulphide bonds and that both - SH and - CHO groups can play only a minor role in the production of bonds which prevent the collapse of stretched fibres on the subsequent treatment. McMahon and Speakman[54] utilized the setting reaction as an index of damage for exposed fibres and followed the fundamental changes occuring in single fibres or groups of fibres, without recourse to treatment of large masses of treatment. Fine fibres suffered more rapid attack than coarse, and natural pigmentation afforded some protection against sunlight damage although removal of the more soluble proteins and reduction of the ash content of the fibres did not affect the rate of attack. Loosely bound water played a more important role in photochemical breakdown than the firmly bound water absorbed at low humidities. Support for the view that the primary photochemical process occuring in wool fibres is one of hydrolysis, was obtained by irradiation at various humidities.

McCann[55] while studying the effect of different wavelengths on the degradation of wool suggested that degradation of the fibre is initiated by radiation of wave-length 2537 A, but after it had started, longer wave-lengths could have an effect. The degradation commences probably at the outer surface perhaps in the scales and proceeds steadily inwards as exposure continues, leading to a more porous structure in the fibre.

Moimaroglou[56] concluded that the diffusion of a dye is more rapid in the irradiated fibre probably due to their more porous surface. He also said that there was some evidence that the longer wave radiation counteracts the action of short wave radiation and that the modification is caused by both short and long wave radiation, each acting independently.

1.09 - Cotton

With cellulose the rupture of the chain molecule by the ultra-violet irradiation involves single bonds of either carbon-carbon or carbon-oxygen. The energy required for both these changes appears to be of the order of 80-90 kg. cal. per mole.[57]

It has been clearly established[8-11] that when dyed and undyed textile materials, including cotton, are exposed to sunlight behind glass (i.e. to light of wavelength greater than 3400 Å), there is neglogible degradation in the absence of oxygen. Egerton and Guirguis carried out some experiments to study the effect of light from a Vistan quartz mercury vapour lamp, having over 96 per-cent of the radiation emitted of wavelength 2537 Å. In most cases it was found that the comparative effect of oxygen and inert gases on the extent of degradation of cotton depended on the particular property of the cellulose used to study the degradation. Using measurements of tensile strength as the criterion, the difference between exposure in oxygen and carbon dioxide was slight. There was a somewhat larger difference with measurements of fluidity and copper number, and with these criteria the degradation in carbon dioxide was approximately two-thirds of that of oxygen. There was also an increase in the carboxyl content of cotton irradiated in carbon dioxide or nitrogen; a still larger effect was observed on exposure in oxygen.[58]

Stillings and Van Nostrand[59] observed the production of carbon dioxide and carbon monoxide on irradiation of cotton in nitrogen. The formation of carboxyl groups may be a preliminary step in the reaction leading to the liberation of carbon dioxide from the cotton. The source of carbon monoxide is presumably aldehydic (or ketonic) groups present in the cellulose. The results of experiments in which cotton was irradiated in the atmosphere of dry and moist nitrogen suggested that the presence of water vapour under these conditions had no influence on the various properties of the cellulose, such as loss in tensile strength, copper number, fluidity and Methylene Blue absorption.

The lack of effect of oxygen and the inhibiting effect of water vapour show that oxidation and hydrolysis, the expected reactions, do not play a predominant part in the photochemical reaction of cellulose in the far ultra-violet. In the near ultra-violet however these reactions have been stated to assume a dominant role.[60] When a light source that includes both of these regions is used, it is reasonable to expect a mixture of effects. This may explain why Stilling and Van Nostrand[59] using a G.E. Quartz Uniarc (model UA26A2), which has about equal output in the near, middle and far ultra-violet regions,[61] did not observe the effects peculiar to each region. Again when tests were made on cotton linters exposed to radiation from a mercury arc lamp with different filters, the degradation effect did not seem to be limited to any particular wavelength but increased towards shorter wavelengths in the vicinity of 2500 Å.

Water vapour was found to retard the decrease in α-cellulose and the depolymerisation of cotton cellulose during irradiation in the far ultra-violet, and the retardation occured with, or without the presence of oxygen[7]. The retarding by water vapour in the far ultra-violet was ascribed to inter-chain water bridging with the hydroxyl group on carbon atom 2 or 3, thus interfering with the freedom of displacement of the carbon atom. It was also found that only one photon out of thousand, at wavelength of 2540 Å, encounters conditions favourable for a rupture of the cellulose molecular chain. Evidence has been presented to substantiate the theory that certain wavelength regions in the spectrum may interact in such a manner as to reduce to a net value the gross degrading effect of the total incidental radiant energy on cotton cellulose. Thus clear glass has a slightly greater protective effect when used to screen a sample of cotton fabric from carbon arc radiation than does blue glass even though the latter has a lower transmission throughout the spectrum.

In studies of the properties of photosensitizing dyes Kautsky[62] paid particular attention to the quenching of luminescence of the basic dye Acriflavine. Both Acriflavine and Acridine orange LP increased the photochemical degradation of cotton in both dry and humid air, although to a smaller extent than the active vat dyes. One of the most important features of the degradation of textile materials by light of wavelength greater than 3400 Å, is the property possessed by many dyes of accelerating the rate of degradation. Certain vat dyes e.g., Caledon Yellow 5G (I.C.I.) and Cibanone Yellow R (C.I. No. 1170) are capable of increasing the rate of tendering of cotton to a large extent. The role of acid, direct cotton and sulphur dyes towards degradation of cotton, silk and nylon was also investigated and all these dyes appear to have the photosensitising effect.

A general scheme of the mechanism involved in the photosensitisation has been suggested[10,11,12] in which the energy absorbed by a dye or pigment under irradiation is transferred to the oxygen in the surrounding atmosphere with the production of activated oxygen. In the presence of water vapour the activated oxygen is assumed to react with the formation of hydrogen peroxide. The photodegradation of cotton or other cellulosic material caused by the formation of hydrogen peroxide has been explained in the following manner.[57] Under the influence of radiation of wavelength less than 3700 Å, hydrogen peroxide is decomposed by the reaction --

$$H_2O_2 + h\nu \longrightarrow 2OH$$

The ultimate decomposition products of the photolysis of hydrogen peroxide are water and oxygen, and the chain mechanism of the photolysis is apparently propagated by the reactions --

$$HO + H_2O_2 \longrightarrow HO_2 + H_2O$$

$$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH$$

Possible reactions by which chains may be terminated are --

$$HO + HO_2 \longrightarrow H_2O + O_2$$

$$2\ HO_2 \longrightarrow H_2O_2 + O_2$$

Consequently, in the interaction of hydrogen peroxide and organic acceptors in the presence of light, there is a possibility of the formation of hydroxyl and HO_2 radicals, and these may take part in the oxidation of the textile materials.

The degradation of pigmented cotton is increased considerably by the presence of either zinc oxide, zinc sulphide or titanium dioxide, but not by zinc carbonate.

It is presumed that this different sensitising property could be attributed to the observation that zinc carbonate is transparent to wavelengths below 3800 Å.[69,6]

It was found by Egerton[58] that the loss in strength of cotton exposed to ultra-violet light was further increased if the cotton was given a boiling treatment with a soap solution after irradiation. This treatment, however, decreased the fluidity of highly tendered cotton. It would seem likely that much of the photochemical degradation of cotton by shortwave ultra-violet radiation occurs near the end of the cellulose chain, possibly in the section containing the potentially aldeydic group. It was observed by Egerton that the degradation of cotton that has been irradiated in nitrogen or carbon dioxide was increased by storage in the dark for a period of several weeks. It would appear that considerable degradation of the textile fibre occured in the absence of oxygen, but depending upon the particular textile fibre, further degradation might result as a consequence of the presence of oxygen in the surrounding atmosphere. The photochemical degradation is accompanied by the drop in the degree of polymerisation and the α-cellulose content.

1.10 - Regenerated Cellulose Fibres

In the case of regenerated cellulose fibres, the result of the photochemical degradation has been suggested as a form of hydrolysis.[65] The glucosidic 1,4 - linkage is split and the aldehydic groups formed are, in the delustered fibre, further oxidised to carboxyl groups, the titanium dioxide acting as an oxidation catalyst. This further oxidation does not appear to take place in lustrous fibres.

The action of light on viscose rayon, both matt and lustrous, was studied by Kleinst and Mossmer,[66] the effect being more harmful in case of the matt fibre; the degree of tendering increased with the fibre fineness. Contamination of the textiles with acids, as well as acid groups formed by oxidative reaction in the cellulose material itself increased the degradation. In the presence of titanium dioxide pigment the sulphur in the acidified fibre is easily oxidised to free sulphuric acid resulting in increased degradation.

Experiments[67] carried out at pH values of 3, 5, 7, 9 and 11 have shown that metals such as copper and, in particular, iron, have a catalytic effect on the photochemical degradation. It was suggested that this effect could be largely eliminated by conversion of salts into insoluble precipitates or by the formation of a salt complex.

Schwen[68] found little difference, on an average, between the dry tensile strengths of the irradiated bright and dull viscose rayon yarn, but when the degree of polymerisation was used as an index of the deterioration, the viscose rayon which had not been delustred proved superior in some respects.

Samples of bright viscose rayon, undyed and dyed, were exposed to sunlight and the amount of radiation was measured on a specially constructed instrument (tin-caesium photoelectric cell and electro-magnetic recorder).[69] After each exposure period, samples were tested for loss of strength. A definite relation between the degree of degradation and the amount of radiation was established. Dyed samples were more resistant to sunlight exposure, the resistance being greatest with dyes that were fastest to light. The products of photodegradation of cellulose were considered to increase the reflection of the fabric in the ultra-violet region, thus protecting it from the effect of radiation.

Irradiation of regenerated cellulose (Cellophane films) with ultra-violet rays was found to result in the rupture of glucoside linkages, whereby part of the absorbed light quanta produced oxidation of alcholic groups. The rupture of glucoside bonds led to the formation of luminescent centres associated with the C = O groups and with increasing number of these groups, the luminescence maximum shifted in the direction of the longer wavelengths. These results led Zapolskii[70] to the conclusion that C = O group present in cellulose initiates the photochemical reaction.

The optical density of films of cellulose and cellulose acetate films increased much more when irradiated in the presence of nitrogen than in oxygen;[71] for nylon the reverse was the case, the optical density being increased to somewhat more after radiation in oxygen than in nitrogen.

Reid[72] expressed the weathering of cellulose acetate in terms of the change in the lustre of the material, and attributed this to its photo-chemical degradation, although no difference was found between the acetyl content, dye content, and viscosities of cellulose acetate in the exposed and unexposed portions.

1.11 - Synthetic Fibres

Most polymers are degraded by irradiation and Roberts[73] suggested that fibres containing aromatic groups e.g., Terylene were relatively resistant, whereas cellulosic fibres, which do not contain any such groups, were extremely susceptible and degraded easily.

It was shown by Vinoa[74] that light and other atmospheric conditions activate the polyamide molecule, and that the hydrolysis of the amide groups results in new amino and carboxyl groups and also in the formation of double bonds and peroxides. It was also shown that during a hundred-day exposure, the molecular weight of the polyamides was reduced and that fibres containing titanium dioxide depolymerised to a greater extent than fibres without titanium dioxide. Ford[75] reported on the formation of an absorption centre at 2900 Å, in nylon by the action of ultra-violet light and suggested that the processes involved free radicals and that the centre was either on the alkyl, or acyl, peroxy radical.

The rupture of the chain molecules of nylon (and silk fibroin) will involve the scission of either carbon-carbon or carbon-nitrogen single bonds. Carpenter[76] found that when monolayers of stearanilide, benzyl-stearylamine, and β-phenylethyl-stearylamine were irradiated with radiation of wavelength 2537 Å, these substances underwent photolysis at the CO - NH linkage. The suggestion was made that proteins containing amino-acids with light-absorbing side-chains might undergo breakage of the adjacent CO - NH linkages in an analogous manner. The energy required for this change appears to be of the order of 80 - 90 kg. cal. per mole.[57]

Investigating the degradation of nylon filament by ultra-violet irradiation, Kato[77] suggested that it was highly probable that ultra-violet irradiation would give rise to photo-oxidation of nylon polyamide chains. This will result in the formation and accumulation of certain aldyhydic substances as relatively stable intermediates with which Procion Black HGS could combine under weak alkaline conditions by virtue of some reactive groups, presumably amino groups, existing in its own molecules.

The electronic spectra have been obtained for a number of irradiated polyamides (including nylon 6.6 and nylon 6.10) and monomeric amides. These spectra indicated that both free radical species are produced as primary products.[78]

Egerton and Filton[79] exposed undyed films of nylon and methylmethoxy nylon to the effect of radiation. They found, after prolonged exposure to a high-pressure mercury-vapour lamp (G.E.C. Osram), in either oxygen or nitrogen, only slight changes in absorption spectra, either immediately after exposure, or after storage in the dark at room temperature or at 50°C; further that on exposure to a low-pressure mercury lamp emitting mainly at 2537 Å, profound changes were produced in the films. These changes were (a) an effect shown immediately after exposure, and (b) a post-irradiation effect which appears on storage in the dark and was greater on storage at higher temperature. The results with the undyed films suggested that on irradiation with near ultra-violet and visible light no trapped free radicals were produced in the polymer material, which makes it doubtful whether free radicals play any part in the degradation of textile materials which are exposed to sunlight behind glass.

Lawton et al,[80] and others have reported results which indicated that nylon is primarily cross-linked by ionizing radiation. However Deely[81] et al, concluded from the results of the radiation of nylon that although nylon cross-links, scission must also play an important role, since the degree of cross-linking saturates at a rather low value. Although Little[82] and Schwemmer[83] have reported differences in radiation effects which they have attributed to the presence or absence of oxygen, it must be concluded that the effects of pressure are as notable as the effects of oxygen, and are perhaps more important. The scission-to-crosslinking ratio of nylon irradiated in nitrogen is almost twice that for nylon irradiated in vacuum. The more rapid deterioration of tensile properties in nylon irradiated in nitrogen was further proof of this effect.

Hydrogen was the principal product from nylon irradiated in vacuo while methane was the predominant product in nitrogen irradiation. Paper chromatography of nylon has consistently shown that greater amounts of amines were present in the irradiated nylon than in normal nylon. The results[84] indicated that scission had occured at all points in the hexamethylene present in hydrolysate of both irradiated and unirradiated nylon. The hydrolysate from irradiated nylon was found to contain all possible primary amines resulting from scission of the hexamethylene-diamine basic unit. Stephenson et al, assumed that the mechanism of irradiation of nylon was based on the reaction taking place in an oxygen-free atmosphere and that the photochemical reaction was a free radical reaction.

Ultra-violet irradiation was reported to cause a darkening of nylon and a gumminess of the surface, by Stephenson et al.[84] They studied the relative efficiency of different wavelengths of ultra-violet light in producing photolytic reaction in polymers when they were irradiated in an inert atmosphere. The surface conditions after irradiation created a large uncertainty in their data. However the irradiation with the three bands of ultra-violet light showed, at least quantitatively, that the shorter wavelength band produced the greater changes in the physical properties and that a threshhold photon energy for damage of nylon could be expected. The experimental results were similar to those reported by Little[85] and Sieman and Bopp[86].

An interesting effect of light on polyamides has been recorded by Achhammer et al[87] who claim an increase in crystallinity after irradiation. The light caused a decrease in molecular weight without a change in basic structure and an impairment of water - and alcohol - resistance.

Scoured and heat set taffeta made from 70-denier 34 filament Amilan yarn (nylon 6) was irradiated for various periods of time in a Fade-O-Meter and the degradation assessed by measurements of intrinsic viscosity number. The average degree of polymerisation decreased rapidly at first, while the amount of water-soluble material increased in proportion to the exposure time. From the above experiments it was deduced by Hashimoto[88,89] that the molecular chain of nylon 6 is split up by light at random.

At somewhat higher levels of irradiation, the ultimate tensile strength and the modulus of elasticity of the undrawn nylon was found to increase while those of drawn nylon continued to decrease until they approximated to nearly the same level. At a still higher degree of radiation the ultimate tensile strength of both drawn and undrawn samples dropped sharply while the modulus of elasticity increased sharply.[90]

Titanium dioxide incorporated in man-made textile fibres by the addition of finely divided pigment to the spinning mixture before extrusion is, however, capable of increasing the photochemical degradation of nylon and cellulose acetate in dry air.[9,10] It appears from the observations that the process of photosensitisation occuring with active white pigment is essentially the same as with vat dyes and dyes of other classes, and involves the formation of activated oxygen and hydrogen peroxide.

The photolysis of polyacrylonitrile[91] has also been investigated using solutions of polymer in a solvent composed of ethylene carbonate and propylene carbonate (80:20 by weight), and by using the polymer in powder and film form. All samples were exposed to ultra-violet light. In solution a random chain-scission reaction took place and at the same time, photochemical reactions occured involving side groups of the polymer chains. Film and powder specimen became crosslinked.

Acrilan deteriorates faster when irradiated in nitrogen than it does when irradiated in vacuum.[84] The more rapid deterioration in nitrogen is in agreement with the higher scission to cross-linking ratio (determined by gel formation) in nitrogen. The difference between vacuum and nitrogen conditions was again indicated in the molecular weight measurements. The molecular weight of Acrilan irradiated in nitrogen changed hardly at all while the molecular weight of Acrilan irradiated in vacuum increased by about 75 per cent.

Little[82] has reported that polyacrylonitrile retains its tensile properties after high doses of radiation better than most polymers. This was in agreement with the data given by Stephenson et al,[84] who also found that the presence of oxygen did not alter the irradiation processes in polyacrylonitrile, as it does in polyethylene and polyamides.

In case of polythyleneglycol terephthalate fibres (Terylene and Dacron), the photochemical processes that take place during irradiation have been attributed mainly to the cleavage of molecular chains (probably C - O linkages).[92] It was pointed out that photochemical decomposition is caused in the first place by ultra-violet rays of the wavelength range 2700 Å - 3400 Å. In this range the polyester exhibits a much greater absorption than any other fibre, showing distinct maxima at wavelengths 2850 Å and 3100 Å. Since this portion of ultraviolet light is to a great extent absorbed by glass, polyester fabrics (curtains) may be expected to possess a much longer life behind glass than on direct exposure.

Gel formation experiments also gave conclusive evidence of different scission-to-crosslinking ratios for vacuum, and nitrogen, irradiated polyethylene. This difference was supported by the different rates of change in tensile properties. The molecular weight of polyethylene irradiated in nitrogen fell quite drastically.[84] Although the work of Alexander and Toms[99] showed quite clearly that the presence of oxygen played an important role in the effect of ionizing radiation on polyethylene, it would appear that the effect of pressure is also important.

EXPERIMENTAL

EXPERIMENTAL METHODS

2.1 MATERIALS.

2.11 - Wool fibres

Experiments were made on wool fibres obtained from a Lincoln fleece. The fibres were steeped in petroleum ether for 24 hours, rinsed, extracted with diethyl ether in a soxhlet for 3 hours, dried and then scoured in a dilute solution of Lissapol N at 60° C for 15 minutes, being finally rinsed in distilled water and dried. Before use all fibres were oven dried at 100° - 110°C, then allowed to condition in air at room temperature for 24 hrs, and then stored in stoppered bottles. The weights quoted refer to the conditioned weight of the material unless otherwise stated. Fibres of approximately similar diameter ($50 \pm 1\mu$) were chosen so that the physical properties of the fibres were as comparable as possible, the root ends and tips being cut off.

2.12 - Wool yarn

The wool yarns used were (a) 30/1 Tex (30/1 worsted) and (b) 148/2 Tex (12/2 worsted). These were cleaned and extracted by the same method as was used for wool fibres.

2.13 - Other fibres

Other fibres used in some experiments were

(I) Matt M 95, 3 denier(Modified viscose rayon)
(II) Bright M 95 3 denier(Modified viscose rayon)
(III) Matt Courtelle, 3 denier
(IV) Acrilan, 3.35 denier
(V) Bright Fibrolane BX, 3.35 denier
(VI) Nylon 66, 210/34 denier yarn.

These fibres were scoured in 2% Teepol solution at 40°C for 2 hrs to remove any soluble added matter before being dried and conditioned.

2.14 - Descaled wool fibres

A device was developed on the basis of that used by Smith[94]. The fibre was fastened between two jaws, which were in turn geared on to two rotating shafts. These shafts were driven by a small electric motor and the centre of the upper gear was on the same level as the upper surface of a flat sheet of glass, the surface of which had been lightly grounded. A mixture of a lubricating oil and a fine optical abrasive powder (200 mesh silica) was applied to this face. The fibre was rotated at a constant speed of 90 r.p.m. A mating piece of polythene 3/4" x 1" was then placed in contact with the fibre and plate, and moved gently along the length of the fibre with combined rotary and translatory motion. At the end of the operation, the microscopic measurement of the diameter of the descaled fibre was carried out. It has been possible to grind lengths up to 3 inches, finishing with descaled fibres of approximately uniform cross section.

2.15 - Method of Exposure.

The fibres were mounted under slight tension on a metal frame, which in turn was mounted on a drum rotating at a constant speed of 55 r.p.m. The fibres were exposed to ultra-violet irradiation for 20, 40, 60, 80, 100 and (in some cases) 120 hours, the distance between the arc and the fibres being 14.5 inches. It was felt that the rotation of the fibres resulted in more uniform exposure, but the time taken for an exposure was not corrected to actual exposure on any specific fibre surface.

2.16 - Temperature and humidity during irradiation.

The temperature inside the cabinet enclosing the frame work was maintained at a constant value of 22°C by the use of a thermostatically controlled heating element and the humidity was maintained at 65% r.h. by the use of saturated sodium nitrite solutions. The uniform distribution of the temperature and humidity inside the whole cabinet was ensured by circulating the conditioned air by means of a fan.

Weekly records of temperature and humidity were kept, using a thermo-hygrograph. These showed that the maximum fluctuations in the cabinet over the period of exposure were of the order of ± 3°C and ± 2 % r.h.

2.17 - Light source

A Hanovia fluorescent lamp model II (80 W) was used for the irradiation experiments. This has a high pressure mercury vapour arc in a quartz tube. The spectral distribution of a high pressure mercury vapour arc is given in Table IV[95]. The figures are averages obtained from data given by several different investigators, whose figures for the individual bands vary by ± 2 % with slightly wider variation for the resonance line 2537 Å.

The total ultra-violet intensity obtained from the S100 source used for obtaining the data in Table IV, was 760 micro watts/cm2 at 24 inches, and 899 micro watts/cms^2 at 18 inches, distance from the source. The calculated intensity at the experimental distance of 14.5in. was 975 micro watts/cms^2.

The intensity of light was checked periodically by means of a spot galvanometer and a sensitive photo-cell.

TABLE IV

(Showing the energy of radiation at different wavelengths)

Wavelength Å	Energy %	Wavelength Å	Energy %
1849,1942	2.0	2753	1.0
2358	0.8	2804	1.3
2378	1.3	2874	1.7
2399	1.2	2925	0.7
2463	0.5	2967	4.7
2483	3.1	3022/26	10.2
2537	6.6	3126/32	19.2
2576	2.3	3341	2.8
2603	0.7	3656/62	28.2
2652	0.7	3906/62	2.6
2699	1.4		

Although this did not give the intensity in absolute units, it did allow a relative check that the intensity was remaining reasonably constant. The use of a uranyl oxalate actinometer - employing the technique of differential absorption spectrophotometry to determine the amount of oxalate photodecomposed, thermopile - galvanometer system[96,97,98] etc was considered to measure the intensity of the ultra-violet light, but the method was not adapted because of the cost and availability of the apparatus required.

2.18 - Test Methods

(a) Strength, extensibility, and work of rupture of a fibre.
(b) Measurement of density
(c) Measurement of refractive index
(d) Measurement of fluidity and viscosity
(e) X - ray diffraction
(f) Alkali solubility
(g) Urea - bisulphite solubility
(h) Water imbibition
(i) Changes in specific surface area of wool
(j) Dye absorption.

(a) Strength, extensibility, and work of rupture of a fibre

The breaking load of a single thread of 30/1 worsted yarn and its extension from an initial tension were determined on a pendulum type single thread testing machine, before and after irradiation. The lower grip attached to the machine drive transversed at a constant rate of 12 inches per minute. The grips were set to accommodate a specimen of 4 inches length. Although this is not a standard test length, this length was chosen because it was the most suited to exposure conditions.

Single fibre strength tests were carried out on a Cambridge extensometer using a constant rate of loading of 1.30×10^5 gm/ cm^2/ min., simulating the test conditions used by Speakman[99]. This necessitated a spring motor ratio of 1 : 9 with a 0.5 oz. spring, and a fibre motor ratio of 9 : 1 the extension being magnified five times. A test length of 4 inches was used, which was suited to give a maximum uniform exposure.

The wool fibres were tested in water and after each extension the fibres were relaxed in water at 20°C for 24 hours to ensure complete recovery and a reproducible stress-strain behaviour. It was later found possible to speed up the recovery of the fibres by using a temperature of 50°C to 52°C as shown by Feughelman[100], whereby a rest of half an hour was sufficient to give reproducible stress-strain curves as long as the extension did not exceed 35 % and the time of total extension did not exceed 10 minutes. The work required to perform each extension was calculated by determining the area between the load extension curve and the extension axis, and the reduction in work found between the unexposed and exposed fibres. This area was the sum total of the areas calculated from the square, triangle, rectangle or trapezium shaped by the curve, a planimeter not being available at this time.

All fibres, other than wool, were tested in the conditioned state, the mean strength and extension being found before and after irradiation, and the results expressed in the reduction in work of rupture.

Load - extension curves of nylon 6.6 yarn were found on an Instron strength testing machine with a test length of 2 inches. A constant rate of extension was used with a cross head speed of 2 in./min. and the chart speed of 5 in./min. The loss in strength of the yarn, after the exposure to ultra-violet irradiation, was expressed as the reduction in work to rupture the yarn, the work done being given by the area subtended by the load extension curve over the extension axis.

All the experimental points shown were the mean of at least 20 replica tests, for all the fibres.

(b) Measurement of density

A simple technique[101] was adopted for establishing a column of liquid graded in density. Fig. 1 shows a simple apparatus, wherein upon subjecting the empty column to reduced pressure the low density liquid (xylene $\rho = 0.862$) was drawn through cock B and replaced in the chamber by the high density liquid (carbon tetrachloride $\rho = 1.594$) from the beaker C. A gradual and even increase in the density of the liquid in the chamber and therefore of the liquid drawn into the column, was ensured by continuous mixing of the carbon tetrachloride and xylene by an electro-magnetic stirrer D, situated below the mixing chamber E. When the vertical tube was filled cock B was closed and the column was ready for use as a means of density measurement. The time taken to establish the column was about 12 min., being controlled by the rate at which the solution was allowed to enter the base of the column. This method has the advantage of taking much less time to establish the column, and overcomes the uncertainties and empiricism of the diffusion method[102] of setting up a liquid column of graded density.

The total intended volume of the column was calculated as 1.6 litres so that 800 ml. of both xylene and carbon

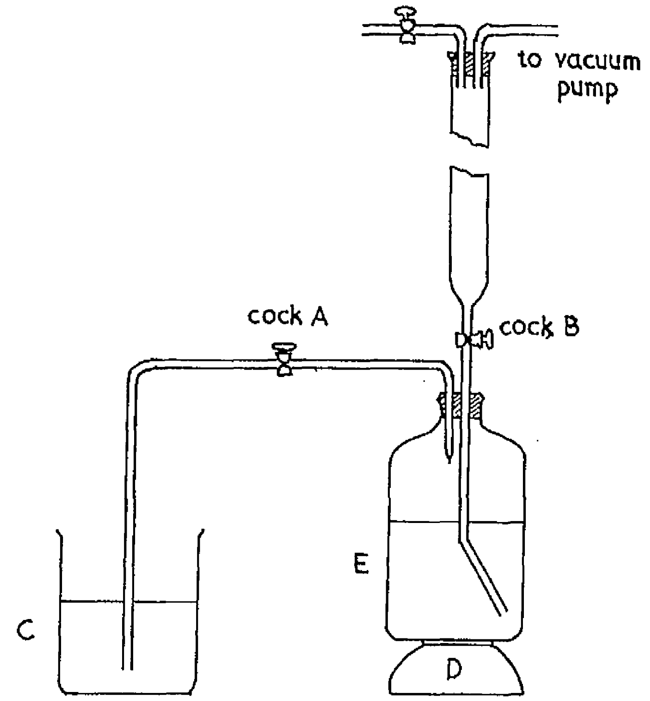


FIG. 1 - Apparatus used for setting up a liquid column graded in density

tetrachloride were taken initially in the outside beaker and mixing chamber E respectively. The density at the base of the column was always less than that of the initial high density solution. The total height of the column was about 100 cm. A dehydrating head containing phosphorous pentoxide was placed over the column to ensure the absence of moisture which might otherwise have an access to the inside of the graded column. Both the liquids used were dried before filling the tube. Sodium wire was used as an drying agent for xylene, whereas carbon tetrachloride was first treated with calcium chloride for 24 hours, filtered and then distilled twice to ensure proper drying.

Before the fibres were admitted, they were boiled in Xylene solution for a few minutes and then immediately transferred into the tube. This ensured that no entrapped air was present.[102]

The density gradient of the column was checked by the use of glass beads which were prepared to cover the range of densities involved.

To facilitate the selection of the required glass tubing of particular thickness for one particular density, a theoretical relationship was derived as follows:

Fig.2 represents a glass bead whose length = ℓ cm., inner axial radius = r_1 cm., outer axial radius = r_2 cm.

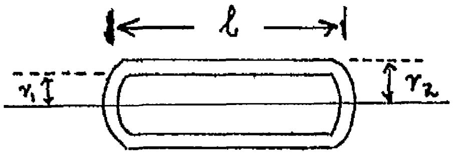


Fig. 2

Then, Volume of bead $= \pi r_2^2 l + 4/3\ \pi r_2^3$ c. cm

and, Mass of bead $= \pi (r_2^2 - r_1^2) l \quad \rho_g + 4/3\, \pi (r_2^3 - r_1^3)\ \rho_g$

approx.

so that, Density of bead $= \dfrac{\text{Mass of bead}}{\text{Volume of bead}}$

$$\rho = \rho_g \quad \frac{\left\{\left[1-\left(\frac{r_1}{r_2}\right)^2\right] l + 4/3\ r_2 - 4/3\ r_1 \left(\frac{r_1}{r_2}\right)^2\right\}}{l + 4/3\ r_2} \qquad \text{-- (A)}$$

$$\rho = \rho_g \quad \left[1-\left(\frac{r_1}{r_2}\right)^2\right] \quad \text{approx. if wall is thin} \quad r_1 = r_2 \qquad \text{--(B)}$$

Where ρ_g is the density of glass

Effect of length on the density of the bead

Assuming $l = 10$ mm., applying this to equation (A)

$$\rho = 2.5 \frac{\left[(1-0.48)\ 10 + 4/3 \times 2 - 4/3 \times 1.386 \times 0.48\right]}{10 + 4/3 \times 2}$$

$\rho = 1.38$

This seemed to be near enough 1.3 in view of the approximation made.

If $l = 20$ mm., then

$\rho = 1.34$ i.e., l has only a second order effect on the density of the glass bead.

So that the density of the bead depends mainly on the ratio of the internal to external diameter and on the density of the glass of which it is made. By taking tubings of different suitable thickness, the theoretical density of various glass beads was calculated after applying the value of r_1 and r_2 in the equation (B).

Finally the above beads were calibrated for their correct density which is given by

$$\text{density of bead} = \frac{M_a}{M_a - M_w} \quad \text{g/cc.}$$

where M_a = weight of bead in air

and M_w = weight of bead in water.

The calibrated beads were introduced into the graded column after drying in acetone, and their positions noted, by means of a cathetometer, along the height of the column. A density profile of the whole column was then prepared.

(c) <u>Measurement of refractive index</u>

The refractive index of conditioned wool was determined by finding an immersion liquid of the same refractive index, the index of this liquid then being measured on an Abbe type refractometer. The Becke line method[103,104] was used in order to discover when the indices of the immersion liquid did match. When the polarizing microscope was defocussed by increasing the specimen - objective distance , a bright line was seen moving towards the medium, either fibre or immersion liquid, of higher refractive index and by decreasing the specimen - objective distance the opposite effect was obtained. Two determinations were carried out, one with the polarizer set parallel, and the other with the polarizer set perpendicular, to the fibre axis.

In order to cover a wide range of refractive index immersion liquids usually consist of a mixture of two stable and non-volatile liquids that do not effect the fibre. Hermans [105] recommends mixture of butyl stearate (index 1.445) and tricresyl phosphate (index 1.558) for cellulose, Faust [106] found a mixture of liquid paraffin (index 1.482) and α- bromonaphthalene (1.658) suitable for nylon and the same two liquids were used by Meredith [106] for cotton. In the present measurements the immersion liquids used in case of wool were same as used by Faust and Meredith, for nylon and cotton, and various mixtures with intervals of 0.001 in refractive index were firstly prepared. After further examination this interval was narrowed down still further until the refractive index of liquid and fibre matched. Care was taken that the temperature of the immersion liquid on the microscopic slide which is in contact with the specimen was same as on the prism of the refractometer, the temperature being 21°C.

(d) (i) Fluidity of Viscose rayon

The standard method[107] of test for the fluidity of viscose rayon in cuprammonium hydroxide was followed in case of Matt M.95 and Bright M.95. However due to the experimental difficulties in exposing a sufficient weight of fibre, a 0.5 % solution was used instead of a 2.0 % as prescribed.

A weighed sample was dissolved in a standard cuprammonium solvent, in a standard capillary viscometer and the rate of flow measured of the solutions of samples exposed for different intervals of time.

The fluidity is given by the equation

$F = \frac{c^1}{t - k/t}$ where c^1 is the viscometer constant, t is the time taken in seconds for the solution to fall from one meniscus to other and $k = 0.131\ V\ t_g$

t_g = time of flow of the glycerol solution,

V = Volume between two marks.

k/t, being very small compared with t, was neglected, so that the fluidity was given by the equation $F = c^1/t$.

(ii) Viscosity of nylon

A method[108], using m - cresol as a solvent was adopted. 0.67 gm of nylon were dissolved in 100 ml. of commercially pure solvent below 50°C in a flask. The dissolution of nylon was ensured by shaking in the stoppered flask for several hours. The resulting solution was filtered through glass wool and the viscosity was measured in an Ostwald type viscometer. The time taken for m - cresol was first determined, the tube rinsed out with nylon solution in m - cresol, and the viscosity of nylon solution in m - cresol then determined by the following equation.

The intrinsic viscosity $V = \frac{\log_e N/M}{C}$, where

N = time taken for nylon solution in sec.

M = time taken for m - cresol in sec.

C = concentration of nylon solution in gm/c.c.

The viscosity is thus expressed in units of decilitres per gm. $\left(dl/_{g}\right)$[87 152]. Nylon samples were irradiated at various times of exposure and the respective viscosities determined. The viscometer was kept in a water bath maintained at a temperature of 20°C ± 1.

(c) X - ray diffraction

Photographs of wool, before and after irradiation, were taken using Ni - filtered Cu K radiation of wave length 1.54 A from a Philips sealed - off tube run at 40 kV and 20 mA. The specimen to (flat) film distance was 4.0 cm.

(f) Alkali solubility

Alkali solubility values for wool were obtained by following the method of Harris[109]. The wool sample, whose initial dry weight was known, was treated with 0.1 N sodium hydroxide solution at 65°C for one hour, the ratio of wool to solution being approximately 1 : 100 by weight. The wool was recovered on a Buchner funnel, washed with water till free from alkali, dried to a constant weight at 105°C, and the loss in the weight determined. Because of the limitations encountered in exposing enough quantity of wool fibres at a time, necessary to make an appreciable liquor ratio, tests were carried out with a yarn rather than a single fibre.

The alkali solubility is the loss in weight expressed as a percentage of the original dry weight of the sample.

(g) Urea - Bisulphite solubility

The method followed for the urea-bisulphite solubility test was that used by Lees and Elsworth[110,111], but with slight modification. Because single fibres were being examined, the method of treatment was amended so that the solubility of single fibres could be determined. The conditioned fibres after weighing were wound over small caterpiller[112] tubes for ease of handling and identification, and were then introduced into a conical flask, containing 50 ml. urea-bisulphite solution (50 % urea + 3 % sodium bisulphite) at pH 7. The flask was immersed in a water bath thermostatically controlled so as to give a temperature of 65 ± 1°C inside the flask, the water in the bath being circulated by means of a propeller to ensure uniform temperature.

After one hour the contents of the flask were poured out into a sintered glass filter and the liquid removed by suction. The residue was washed 3 times with 25% urea solution and at least 6 times with distilled water and dried at 105°C till a constant weight was reached. The loss in weight of the unexposed and exposed samples in urea-bisulphite was calculated. The fibres were weighed on a Shirley microbalance which could read accurately to the 5th decimal of a milligram and gave results up to the accuracy of ± 1.5%. The pH value of the solution has been shown to be a very critical factor and the maximum solubility occurs at pH 7. The pH of the urea - bisulphite solution was adjusted by adding approximately 2 ml. of 5 N sodium hydroxide per 100 ml. of the reagent.

(h) Water Imbibition

Cameron and Morton[113] define *imbibition value* as the quantity of water, in parts per 100 parts of dry fibre, retained by the wet fibre after centrifuging a 0.5 gm sample for 5 minutes at 1000g. This value is a very close approximation to the amount of water taken up within the substance of the dry fibre when it is swelled to equilibrium on immersion in water.

In the present test, samples of unexposed and exposed wool were placed in sealed tubes containing distilled water which were mechanically agitated for 24 hours to ensure perfect soaking and thereby reach the equilibrium, after which these were transferred to 15 c.c centrifuge tubes[113,114] . These were then centrifuged at 2000 g., for exactly 15 minutes in a Fielden Walker centrifuge. The speed required will depend on distance of the sample from the centre of the centrifuge in the particular instrument used. This was measured and the speed calculated from the simple formula $N = 298 \sqrt{F/R}$

where F = gravitational factor

R = the distance of the sample from the axis in centimeters

and N = the number of revolutions/min of the centrifuge

The number of revolution per minute was approximately 3000. After centrifuging the tubes were withdrawn one by one from the instrument and the samples introduced without delay into stoppered bottles whose initial weight was known. The samples were given no opportunity to lose moisture to the atmosphere. After drying to a constant weight at 110°C, they were weighed and the ratio $\frac{\text{absorbed water}}{\text{dry weight}}$ calculated.

(1) Specific surface area of wool

Giles et al[115] have found solution absorption of p-nitrophenol at room temperature to be suitable for specific surface area measurements on a wide variety of solids, including carbon, cement, coal, fibres, organic pigments and water soluble materials e.g., sugar. The experimental procedure was as follows.

p-Nitrophenol was recrystallised from water and 500 ml. of 40 m.mole/l. p-nitrophenol solution was prepared, using water (demineralised) as a solvent. Eight ordinary soda glass test tubes (5/8 in. diameter) were taken and 0.05 gm. of finely cut wool yarn was weighed in these accurately. Into each tube was then placed 10 c.c of the mixture of p-nitrophenol solution and water in a range of concentrations 1 m.mole/litre to 40 m.mole/litre of p-nitrophenol. All the addition of the solutions were made from a micro burette, and were preceded by drawing of the tube near the top. The tubes were then sealed in a flame and fixed by phosphor - bronze spring clips to a shaft mechanically rotated at 35 r.p.m. under water in a thermostat tank, at room temperature (18-19^{0}C), in order to give constant end-over-end agitation (Clunie and Giles, 1957[112]). After 24 hours, by which time the absorption equilibrium had been reached, the tubes were allowed to stand till all the wool fibres settled down, the supernatant liquor then being decanted. A blank set was also done without any wool, to get the calibration solutions.

Dilution and analysis

1 ml. of p-nitrophenol solution from each of the above tubes was diluted in different order. Before making up the total volume by dilution, different amounts (0.5 - 2 ml) of 10% sodium hydroxide solution were added, depending upon the dilutions made. This was to make sure that the solution was alkaline. All these aqueous solutions were measured on a spectrophotometer (Unicam SP 600) at 4000 Å, using a 5 ml. cell. The dilutions were made in such an order as to give the optical density on the spectrophotometer between o.3 to 0.7, the range in

which it reads most precisely.

Wool, exposed to ultra-violet irradiation for different intervals of time, was treated the same way. Isotherms were drawn between m.mole/litre p-nitrophenol in the resulting liquor and m.mole/kg taken up by the fibre, and from these the specific surface area calculated.

(j) Dye Absorption

Unicam spectrophotometer (type SP600) was used to measure the optical characteristics of various extracts over a wider range of wavelengths than is possible with the EEL apparatus.

In attempts to make quantitative measurements of the absorption of Methyl orange, the samples of wool fibres were weighed and immersed in dye solution in sealed test tubes, which were agitated mechanically in a thermostatically controlled water bath for two hours. The tubes were then removed, broken open and the partially exhausted dye liquors were measured absorptiometrically. From the optical densities so obtained absorption isotherms were drawn.

EXPERIMENTAL

RESULTS

3.1 - STRENGTH, EXTENSIBILITY AND WORK OF RUPTURE

Figure (3) shows the relation between the time of exposure and percentage loss in strength and extension of a 30/1 worsted yarn. It can be seen that the increase in exposure time brings about an appreciable loss in tensile properties of the yarn, the effect being more drastic towards increasing the loss in extension than towards increasing the loss in breaking strength.

The load extension curves obtained by Engeler[116] when testing wool fibres with the Schopper Fibre Dynamometer were divided by him into three parts, viz (i) in which extension of the fibre is proportional to load (ii) in which the extension increases out of proportion to the increase in load (iii) in which extension is less per unit load increase than in (i). Section (i) contained the interval up to the limit of elasticity, section (ii) the region of plasticity and section (iii) the region of deformation up to the breaking point. The area enclosed by the curve and the abscissa is a measure of the work done in breaking the fibre. Tests carried out on wool which had been damaged as uniformly as possible by the action of light indicated that the greatest difference lay not between the strength and extension, but between the relative amounts of work done in breaking them.

Wool fibres show an appreciable loss of energy apparently increasing with the time of exposure. The graph (Fig. 4) plotted between the time of exposure and the percentage reduction in work of rupture shows an exponential relationship, the greatest degradation occuring up to an initial 60 hours exposure.

Figure (5) shows the effect of exposure time on the percentage reduction in work of Acrilan and matt Courtelle. In Courtelle most of the degradation appears to be occuring within 40 hours exposure. There appears to be a distinctive difference in the rate of attack on Acrilan and matt Courtelle, although both are acrylic fibres. This might be of interest in view of the fact that acrylics are stated to have a higher resistance to light than most of other fibres, but as one fibre was delustred and the other one bright, the difference in their resistance to ultra-violet light (16 per cent at 60 hr. exposure) may be due to the presence of a delustring agent in one.

Figure (6) gives a relationship between the exposure time and the percentage reduction in work of Matt M95, Bright M95 and Fibrolane BX. Up to 40 hours exposure to ultra-violet light, the degree of degradation in descending order of severity seems to be Fibrolane BX, Matt M95 and

Bright M95, whereas above 60 hours exposure Bright M95, Matt 95 and Fibrolane BX seems to be damaged in that order. Here also the effect of delustring agent is quite pronounced as up to 60 hours exposure Matt M95 suffered 8 per cent more reduction in work than Bright M95.

Figure (7) shows the percentage reduction in work (up to the breaking elongation) of nylon 66 yarn, 210 den., plotted against the time of exposure. It seems from the graph that nylon suffers a greater loss in strength for the initial 30 hours exposure, after which there is a steady but reduced rate of degradation. The effect of ultra-violet exposure on the tensile strength is shown in the Table V.

TABLE V

Exposure time hr.	Breaking extension in.	Breaking load kg.	% Extension	% Reduction in Work
0	0.412	1.282	20.6	0.0
20	0.349	1.141	17.5	32.9
40	0.304	1.001	15.2	45.6
60	0.301	0.982	15.0	52.1
80	0.281	0.894	14.0	58.9
100	0.266	0.793	13.3	66.9

3.2 - Density and Refractive Index

Figure (8) shows a density profile, in a liquid column formed from xylene and carbon tetrachloride, which seems to be practically linear, Figure (9) shows the increase in the density of wool fibres with the increase in exposure time to ultra-violet irradiation.

As a check on the density measurements,[117] the determination of the refractive indices of exposed and unexposed samples were carried out. The high molecular weight of the immersion media and their nature seemed to guarantee that they were still less capable of penetrating into the fibre substance than the liquids used for density measurements. The results are given in Table (VI). Each

TABLE VI

(The changes in density and refractive indices of wool with ultra-violet irradiation)

Exposure time hr.	n_{11}	n_{1}	n_{iso}	d	$\frac{n_{iso}-1}{d}$	$n_{11} - n_{1}$
0	1.5510	1.5407	1.5441	1.3200	0.4122	0.0103
20	1.5516	1.5415	1.5449	1.3245	0.4114	0.0101
40	-	1.5420	-	1.3280	-	-
60	1.5525	1.5423	1.5457	1.3320	0.4097	0.0102
80	-	1.5426	-	1.3340	-	-
100	1.5535	1.5430	1.5465	1.3360	0.4091	0.0105

reading in the table of the density and the refractive indices is the mean of 5 experimental readings. The refractometer used is considered to read accurately to the third place of decimal, the fourth place value being obtained on summation of results.

In Table (VI) n_{11} and $n_{\perp}$ are the refractive indices, d is the density and $n_{11} - n_{\perp}$ gives the birefringence.

In case of anisotropic fibres, the two principal refractive indices are determined separately and the isotropic refractive index calculated from them by the equation

$$n_{iso} = 1/3 \left(n_{11} - 2n_{\perp} \right)$$

Let us consider the results of density determination in organic liquids and determination of the refractive index. The well known rule of Gladstone and Dale states that if n be the refractive index of a substance, then $\frac{n - 1}{d}$ is a constant independent of temperature.[118] If we multiply this by the molecular weight M, we obtain the molecular refraction M R, which could be found additionally from known atomic refraction.

The fibre substance must be considered as compact and as consisting of a practically homogeneous mixture of crystalline and amorphous parts. It then must be expected that there is a definite relation between refractive power and density of a fibre.

It is seen from the experiments that the corresponding change in refractive index is smaller than the increase in density after ultra-violet irradiation of wool. The birefringence seems to be practically unchanged after irradiation. Hermans[105] concluded that since the molecular refraction of both native and regenerated fibres appeared to be same, and since the quantity of crystalline matter is very different in both cases, the applicability of the Gladstone and Dale rule was independent of the percentage of amorphous region.

3.3 - Fluidity of Matt M 95 and Bright M 95

The fluidity measured was that of an 0.5 per cent solution in cuprammonium hydroxide and to give a measure of the standard fluidity, i.e., of 2 per cent solution, a relation between the percentage concentration and fluidity has been drawn (Fig. 10). This relation gives a curve more or less of linear characteristics. It was assumed therefore that for the comparative purposes the fluidity values of 0.5 per cent solutions could be accepted as representative of the degree of degradation of the samples.

Figure (11) shows the effect of ultra-violet light on the fluidity of both Matt and Bright M 95. It is seen that in both fibres the fluidity increases steadily as the time of exposure to ultra-violet light is increased. Although light sensitivity of Matt viscose is reported to be greater than that of Bright viscose, the present fluidity measurements would suggest that the degree of chemical degradation is similar. It can be seen that in the initial period of exposure up to 50 hours the curve for Matt M 95 is steeper, however, it is not statiscally significant.

In general, greater variations in strength losses occured with the Matt sample than with the Bright sample, while in both cases these types of variation in fluidity values after equal period of exposure appeared to be less extensive than was the case with a corresponding strength losses. From the standpoint of practical service, the loss in breaking strength in fibres during exposure to ultra-violet light is usually the most important feature of the damage suffered.

Investigations[129] in the field of cellulose chemistry have shown that when cotton is uniformly degraded by a chemical action such as acid hydrolysis, a definite relationship exists between the resulting changes in its strength and fluidity. Although the action of light on exposed fibres cannot be described as uniform, it still appeared possible that the relationship found to exist between their strength and fluidity changes might throw some light on the mechanism by which the breakdown of cellulose is affected. When fluidities at a particular exposure were averaged and plotted against the corresponding average percentage reduction in work, as shown in figure the resulting relationship was practically linear. (Fig.12).

3.4 - Viscosity of Nylon

The relation between the intrinsic viscosity of nylon samples and the time of exposure to ultra-violet light is shown in(Figure 13). This shows that viscosity is decreased as the period of exposure to the degradation conditions is increased, the fall in viscosity being quite large up to initial 30 hour exposure.

The applicability of Baker's equation[120] $\eta_r = \left(1 + \frac{[\eta]c}{Z}\right)^Z$ to the polyamide solution were examined by Achhammer and his co-workers during their investigations into the mechanism of photochemical degradation of polyamides. The value of $Z = 3$ was found to fit the data adequately. The agreement between the values of intrinsic viscosity (η) obtained for the same specimen but with different concentration was fair. Taylor[121] has expressed the relationship between the intrinsic viscosity of nylon fraction in formic acid and the molecular weight as $M_N = 13000 (\eta)^{1.39}$, where M_N is the number average molecular weight and (η) is the intrinsic viscosity in formic acid. Their measurements of intrinsic viscosity were made in m-cresol, in 90 percent formic acid the intrinsic viscosity values are approximately 0.9 of those determined in m-cresol.

Application of Taylor's relation of intrinsic viscosities of unirradiated and irradiated nylon leads to a viscosity - molecular weight (M_V) given in Table (VII).

TABLE VII

Exposure time hr.	Viscosity-average molecular weight M_V
0	9532
20	5907
40	5140
60	4598
80	3929
100	3757

Figure (14) shows the relation between the viscosity of nylon solution and the percentage reduction in work after different intervals of time, which seems to be a linear one. The possibility cannot be excluded that the viscosity relation of photochemically degraded yarn is a function of the changes in yarn structure.

3.5 - X - Ray Diffraction

On visual observations no marked change was observed in the X-ray photograph of the irradiated wool.

3.6 - Alkali Solubility Test

Wool fibres show an appreciable increase in alkali solubility after exposure to ultra-violet light. The results of those experiments show an approximately linear relationship between the exposure time and percentage alkali solubility of both samples (30/1 Tex and 148/2 Tex). From the graph it is observed that the solubility difference between undamaged wool and wool exposed for 20 hours is greater than the difference between wool exposed for 20 hours and 40 hours (Fig. 15).

As alkali solubility of wool has been used as an index of the chemical damage of wool by different agents, the extent to which a coarse yarn and a finer yarn are damaged is given by the curve A and curve B respectively. For the coarse yarn the percentage alkali solubility increases from 21 to 31 percent during 100 hours exposure. The finer yarn is more easily damaged, the alkali solubility increasing from 20 percent to 45 percent. Thus it seems likely that the degradation moves fairly steadily inwards from the surface of the yarn.

3.7 - Urea - Bisulphite Solubility

The present tests were made to find out the behaviour of wool damaged by ultra-violet radiation towards the urea - bisulphite solution. Damaged samples exposed to ultra-violet radiation for different periods of time were treated with the same solution at pH 7. A graph was plotted (Figure 16) between time of exposure and the percentage urea-bisulphite solubility. The solubility is shown to increase with increasing exposure time, the rate of solubility being higher for the first 30 hours followed by a further increase but with a lower gradiant.

From the results given by Lees and Elsworth[110,111,] it is clear that the pH value of the reagent is an important factor in relation to the amount of wool dissolved, maximum solubility occuring at pH 7. Figure (16) shows the effect of pH on the percentage urea-bisulphite solubility of wool exposed to ultra-violet radiation. While the increase in solubility of wool exposed for 100 hours at pH 5 is from 2.5 to 9 percent, the corresponding increase at pH 7 is from 7 to 28 percent.

Table (VIII) shows the effect of ultra-violet light on the descaled wool fibres when urea-bisulphite solubility is used as an index of degradation.

TABLE VIII

Exposure time hr.	Urea-bisulphite solubility %	
	Intact Wool	Descaled Wool
0	9.74%	35.00%
40	15.60%	20.90%
80	19.23%	17.05%

It is seen that while the solubility of irradiated intact wool increases with increase in exposure time the solubility of the irradiated descaled wool decreases with increase in exposure time.

The values given in the table are the mean of ten experimental readings.

3.8 - Water Imbibition

When keratin fibres from various sources were dried, and immersed in water a diametrical swelling was recorded by Haly.[122] Although similar trend was found for Merino and Lincoln wools, the results indicated that if typical Lincoln and Merino fibres of the same diameter could be obtained, the rate of uptake of water by Lincoln fibre would be approximately twice that for the Merino fibre.

The presence of cross-bonds stable to water is indicated by a marked reduction in the imbibition value. The results of the examination of a series of exposed wools are shown in Figure (17), where the imbition value is plotted against the time of exposure to ultra-violet light. It can be seen that in case of wool fibres the imbibition value decreased from 54 percent in case of unexposed fibres to about 41 percent in case of wool exposed to 100 hours.

3.9 - Specific Surface Area of Wool.

(Sorption Isotherms)

p-nitrophenol from water solution was used to measure the surface area of wool fibres. The value obtained was much higher than the microscopic value[123] (microscope, 10.13 $m^2 g^{-1}$; p-nitrophenol *ca* 48 m^2 g^{-1}). This shows that p-nitrophenol penetrates the internal structure of the fibres, as expected.

Calculation of the Specific Surface Area

In all the cases the isotherm - concentration on substrate (C_s) against concentration in bath (C_B) - were plotted (Figure 18,19) and the monolayer capacity determined from the first plateau of the isotherm. Table IX shows the amount of p-nitrophenol present initially in the solution and that taken up by the fibres, exposed to ultra-violet light source.

Consider the curve A (Fig. 18) which is sigmoid in shape. The specific surface area (S) as given by the following equation

$$S = C_s \times N \times A$$

where C_s = monolayer capacity in moles/gm.

(In this figure curve A, its value is 106 m.moles/kg)

N = Avagadro Number (6.19×10^{23})

A = Area occupied by 1 mole of p-nitrophenol in cm^2

(25×10^{-16} in this case)

As concentration on the substrate in the figure is given in m.moles/kg, it must be divided by $10^3 \times 10^3$ to give concentration in moles/gm.

Therefore $$S = \frac{106}{10^6} (25 \times 10^{-16}) \times 6.019 \times 10^{23}$$

$$= 159 \times 10^3 \ cm^2/gm \text{ or } 15.9 \ m^2 . g^{-1}$$

In practice the values obtained by nitrogen measurements are often taken as absolute. Nakhwa[124] has shown that in most cases the method using p-nitrophenol give results that compare very favourably with those of nitrogen estimation.

TABLE IX

EXPOSURE TIME (HR)	NO.	INITIAL m·mole/ℓ	DILUTION	OPTICAL DENSITY	FINAL m.mole/ℓ	m.mole/ℓ TAKEN UP	m.mole/kg TAKEN UP
	1	4	-	-	-	-	-
	2	8	200	0.327	7.369	0.631	12.62
	3	12	200	0.476	10.730	1.270	25.40
0	4	16	250	0.425	13.940	2.060	41.20
	5	22	500	0.339	19.100	2.900	58.00
	6	28	500	0.432	24.340	3.660	73.20
	7	34	500	0.510	29.300	4.700	94.00
	8	40	1000	0.310	34.930	5.070	101.40
	BLANK	40		0.355			
	1	8	200	0.310	7.166	0.834	16.68
	2	12	200	0.409	10.880	1.120	22.40
	3	16	250	0.507	14.290	1.710	34.20
20	4	22	500	0.394	19.950	2.050	41.00
	5	28	500	0.451	25.410	2.590	51.80
	6	34	500	0.594	30.080	3.920	78.40
	7	40	1000	0.316	35.320	4.680	93.60
	BLANK	40		0.355			
	1	4	100	0.237	3.684	0.316	6.32
	2	8	200	0.336	7.437	0.563	11.26
	3	12	200	0.499	11.250	0.750	15.00
48	4	16	250	0.525	14.790	1.210	24.20
	5	22	500	0.356	20.050	1.950	39.00
	6	28	500	0.452	25.490	2.510	50.20
	7	34	500	0.549	30.590	3.410	68.20
	8	40	1000	0.310	35.830	4.170	83.40
	BLANK	40		0.355			

where values by nitrogen were higher than by p-nitrophenol the reason is that the nitrogen molecule (cross-sectional area of solid and liquid nitrogen are 13.8 A^2 and 17.0 A^2 respectively)[125] is smaller than p-nitrophenol and can penetrate smaller pores in the fibre.

As mentioned earlier, the monolayer capacity was calculated in each case from the first plateau of the isotherm and the Langmuir reciprocal plotting method or B.E.T. equation mentioned under gas absorption was not adopted.[124]

The specific surface areas of the unexposed and exposed fibres are given in Table X.

TABLE X

Exposure time hr.	s.s.a. $m^2.g^{-1}$
0	15.95
20	14.62
40	13.39

No further appreciable decrease in specific surface area was noticed for wool exposed to 100 hours to ultra-violet light.

3.10 - Dye Absorption

Graph (figure 20) shows the absorption spectra of methyl orange solution after 2 hours treatment with unexposed and exposed wool. One can gather by this that with increasing exposure time to ultra-violet light the fibre absorbs an increased amount of the components (red and yellow) of methyl orange. And as there is slight shifting of peaks towards right after successive doses of radiation, it may be that at first mainly yellow component is absorbed by the exposed wool, much more than the unexposed one and then with increasing time of exposure the proportion of red taken up, relative to yellow, increases markedly. This was quite marked by visual observance.

The following experimental results suggest that in the case of ultra-violet irradiation of wool it is modification of the epicuticle which is primarily responsible for the accelerated rate of dye uptake. Pieces of fibres were abraded as described earlier. The pieces were then cut into halves, half was irradiated for 20 hours by ultra-violet light source. The irradiated and unirradiated pieces were immersed in dye (methyl orange and methylene blue) at room temperature on the same microscopic slide and examined at intervals for depth of colour. Both irradiated and non-irradiated pieces appeared to dye at approximately the same rate, and were heavily dyed before an intact fibre on the same slide had acheived any appreciable coloration. It thus appears that ultra-violet light effects rate of dye absorption by the wool fibre cortex, the effect is secondary to modification of the cuticle. These results were very much same as recorded by Haly.[126]

DISCUSSION

4.1 PHOTOCHEMICAL EFFECT ON WOOL

(i) Reduction in tensile properties

If the cross-links in the keratin molecules have been attacked in any way, the work required to stretch a fibre is affected, the change being a measure of the extent of damage.[53] This effect is markedly pronounced after irradiation, since disulphide cross-linking groups are hydrolysed and other changes[18] take place. The relationship between reduction in work and number of disulphide bonds broken is not however, linear because disulphide bonds breakdown is accompanied by intense swelling which itself facilitates extension owing to breakdown of hydrogen bonding between the peptide chains.

Before continuing the discussion on the changes produced in physical characteristics of the wool fibre by ultra-violet irradiation, it is worthwhile to mention here the molecular structure of wool.

(a) Micelle structure

Speakman[127] first advanced a theory of the micellar structure of keratin fibres after X-ray analysis. Alexander[128] suggested that the molecules are held together within the micelle by hydrogen bonds to give rise to crystalline areas in the fibre. The micelles which are supposed to be set in a cystine cross-linked cement are connected to the latter by disulphide bonds. The disulphide bonds within the micelles which are few in number[129] are arranged in such a way as to allow relative movement of the molecules within the micelle. Although no accurate estimate of the proportion of the wool fibre which is truly crystalline is available, this is certainly less than 50% of the total fibre material and it may be as low as 10%.[130] It seems reasonable to suppose that the individual micelles contain crystalline areas in much the same way as synthetic fibre contain crystalline regions, one chain may thread its way through both crystalline and amorphous region giving rise to a structure which is called a fringe micelle.

(b) Fringed Fibril structure

Many of the important features of the fringed micelle structure are combined with fibrillar structure in the "fringed fibril" structure proposed by Hearle.[131] In this structure the fibrils are assumed to be long, perhaps effectively infinitely long, imperfect crystals winding their way through the fibre structure, and separated by non-crystalline regions. As in the fringed micelle structure, long chains are assumed to pass alternately in and out of crystalline and non-crystalline regions linking the two structures together in a continuous manner. It has been suggested that inter-fibrillar material is richer in cystine than the fibrillar material.[132]

Keeping in mind the above structure let us now see how the changes in different physical and chemical properties are brought about by ultra-violet light.

(ii) Physical properties

The results on the density measurements after irradiation show clearly that the structure of the fibre becomes more compact after the degradation.

Hermans and Vermaas[117] have suggested that density might depend on the percentage crystallinity present in the fibre substance. They have pointed out that density and pore structure are macroscopic concepts, whereby it is now known that any free space within the fibre is of molecular dimensions only, arising from the inefficient packing of the bulky side-chains. Thus organic liquids like carbon tetrachloride and benzene cannot penetrate the fibre but merely envelop it completely. In these media therefore, the measured density corresponds to the fibre as a whole, including any free volume within the fibre. When a swelling liquid is used, an increase in density results owing to the filling of such free space by a rearrangement involving more efficient packing of molecules and side chains in the swollen fibre. In order to check this theory, the density of the fibres should be compared with some other relative measure of crystallinity for example the sorption capacity for moisture. The moisture regain of wool is changed during irradiation as observed by Truter and Woodford;[233] Barritt and King,[29] and Cunliffe.[37] Even when the samples are washed after irradiation, the regain increases so that the conditioned samples appear to have lost less than dry ones, but the overall change in regain was still a decrease. Modern views on fibre structure and on the process of moisture absorption lead to the conclusion that, at not too high vapour pressure, the sorptive capacity of the fibre should, at least, to a first approximation be proportional to the percentage of amorphous substance.

The fibre substance must be considered as compact and as consisting of a practically homogeneous mixture of crystalline and amorphous parts. It then must also be expected that there is a definite relationship between refractive power and density of the fibre. This is given by the Gladstone and Dale formula, i.e. that $\frac{n - 1}{d}$ should be a constant for a given fibre.

Our results while showing an increase in refractive indices after irradiation in case of wool fibre also show that the calculated value of $\frac{n-1}{d}$ decreases gradually as the exposure time increases. We have to take an important factor into consideration which is that the wool fibre is never wholly crystalline: there being a certain proportion of amorphous material, having optical properties different from those of the crystals, which is also affected quite appreciably by ultra-violet degradation.

The results of the increase in density, and, to some extent refractive index, suggest some increase in the crystallinity after ultra-violet irradiation. The explanation can be made that along with the disulphide bond breakdown there is a breakdown in the main peptide chains probably by the short-wave radiation. If we take the fringed micelle structure into consideration it is quite probable that after the main chain is broken, along with the degradation of disulphide linkages, the smaller chains will have the tendency to come closer to the region of crystalline order and orientate themselves along that region. As there is no appreciable change in the birefringence after irradiation, no changes in orientation of the crystals as such could be accounted for. So partial crystallisation of the crystallites might occur to make the structure rather more compact, thus giving higher density.

If we take into account the fringed fibril structure, it can be assumed here also that as the long chain molecules which pass alternatively in and out of crystalline and non-crystalline regions are degraded in the latter region, in the sense that disulphide bonds or the peptide bonds are broken, this might result in some chains aligning themselves along the fibril up to a certain length thus increasing the crystallinity of the structure partially. Also it has been suggested that inter-fibrillar material is richer in cystine than the fibrillar material. This is to be expected; the joining together of two protein chains is unlikely to occur at exactly the right positions needed for both chains to be incorporated in the crystalline lattice and so it is probable that portions of molecules, including cystine groups, will be pushed out in the non-crystalline region. So it is quite likely that breaking of cystine linkages by ultra-violet light could make it easy for those chains nearer the fibrils to get aligned to it. All these inferences might lead one towards an idea of increased crystallinity of wool after irradiation. Usually any change in the crystallinity after irradiation should show up in a change in the X-ray diffraction pattern of the exposed wool, but no marked change in the pattern was observed. However, it is significant that most chemical reactions with wool and hair have little effect on the X-ray diffraction pattern unless they are of the type that leads to a dissolution of the H-bonds.[194]

Increase in density due to the products of hydrolysis and oxidation

The reaction which is supposed to take place due to ultra-violet irradiation is primarily that of hydrolysis of the disulphide bond of the cystine linkage in the following manner:-

$$\mathrm{CH - CH_2 - S - S - CH_2 - CH} \xrightarrow{H_2O} \mathrm{-CH - CH_2 - SOH + HS - CH_2 - CH-} \quad \text{(i)}$$

One molecule of water is takenup by $-S-S-$ bond resulting in the increase in weight by the formation of $-SOH$ and $-SH$ group. This increase in weight as calculated per 100 gms of keratin comes to be 0.98 gms (molecular weight of cystine = 240, percentage of cystine in wool keratin = 13.1%). If we suppose that after 100 hours all the cystine linkages are broken and that there is no appreciable change in the spacing of the main chains, then the density of the fibre will increase by approximately 1%. The density of wool fibre after 100 hours exposure increases by 1.2% (Table VI). As the two figures are quite near, the possibility cannot be ruled out that the increases in weight by the products of hydrolysis might be the reason for the increased density.

Further oxidation may occur resulting in the following products

$$CH - CH_2 - SO_3H + HO_3S - \quad \text{(ii)}$$

The increased in weight as calculated in this case would be about 4.8 gms per 100 gms. of keratin. However this value is much higher than the value of increased density got in the results. Thus a possibility of increase in the density of wool by this reaction can be ruled out, further because with the increase of such a mass the change in the internal volume cannot be neglected.

The above suggestions are made with few suppositions and moreover the nature of the stability of the products of reactions (i) and (ii), and their continuity is uncertain. On the other hand the suggestion put forward of an increased crystallinity is supplemented by the results of other experiments.

Chemical Changes

(iii) Water imbibition

According to the general idea of structure mentioned earlier, the molecules of liquid can penetrate between the micelle forming a gel of relatively low water content. The extent of penetration of liquid this way may determine the extent of specific surface area available which in turn will give some idea of the crystalline amorphous ratio of the fibre.

During the swelling of a fibre in water the crystallites remain unchanged, so that the basic fibre structure dependent on crystal forces limits imbibition. With reagents which are able to penetrate the crystallites and so cause unlimited swelling or dissolution of the untreated fibre, the presence of cross-bonds stable to reagents may be expected to limit the swelling. The highly anistropic swelling of wool fibres and similar polymer systems is explained by the association of a limited number of polymer chains into definite units or micelles with their axes orientated almost uniformly parallel to the fibre axis.[127] According to this general arrangement, molecules of liquid can penetrate between the micelles forming a gel of relatively low water content and the extent of penetration of liquid into the micelle may be investigated by finding the imbibition value.

In the case of wool, most of the swelling is known to be inter-miceller as the X-ray spacings are only slightly affected by water absorption.[135,136] When a wool fibre is immersed in water, it absorbs or imbibes approximately half its dry weight of water within the structure, its dimensions, especially transverse, increasing simultaneously. The imbibed water must be accommodated in the amorphous region, and we refer to the average separation distance of the structural units in the swollen fibre as a pore size. From the results we see that the water imbibition, which gives the amount of chemically held water in the pore size, decreases appreciably after irradiation. This could be due to the decrease in the pore size or in other words due to the increase in dimensions of the structural units.

(iv) Changes in specific surface area

The specific surface area of wool fibre is also shown to be decreasing with increase in exposure time to ultra-violet light. This method of physical adsorption of p-nitrophenol is more sensitive, as it gives the total surface area available for molecular absorption including surface irregularities and channels of molecular dimensions within the fibre. This area seems to decrease as the exposure time increases thus hinting at the possible changes in the crystalline element as suggested before.

(v) Dye absorption

As seen in the results the dye absorption increases with increase in exposure time. As there was no appreciable difference in rate of dye absorption after ultra-violet radiation in case of the intact and descaled fibres, it shows that it is the fibre epicuticle which is responsible for the increase and the changes in the epicuticle are independent of the changes in the cortex, and this suggestion is supported by the possibility of difference in the felting properties of wool fibres after ultra-violet irradiation.

It has been known for many years that one of the effects of ultra-violet irradiation on wool is to increase the rate of uptake of some dyes. Other treatments which produce a similar results include modification of wool by alkali, by acid and by chlorination. Lindberg[46] concluded that reaction of alkali and acids with the fibre epicuticle was responsible for the increased rate of dye uptake in these cases.

In an experiment by Haly,[126] intact fibres were treated, for 10 minutes, in a 2 percent wt/vol. butanolic KOH solution. This treatment is believed to affect only a region close to the fibre surface. Some of the fibres were then irradiated. On subsequent dyeing it was found that again the irradiated and unirradiated fibres dyed at approximately the same rate. The epicuticle was destroyed by irradiation. This was demonstrated by the fact that

Allwordon blisters formed on fibres irradiated in saturated bromine water after the fibre had been irradiated. It is seen from the experimental results that while the rate of dye uptake of the irradiated wool fibres increases, at the same time the p-nitrophenol absorption at equilibrium decreases. As explained earlier, the rate of dye uptake is related to the changes in the epicuticle and hence any damage to the epicuticle layer is likely to give increase rate of dye uptake (Figure 20). The decrease in the equilibrium adsorption of p-nitrophenol suggest some kind of change in the internal structure of wool either in way of cross-bond formation or in the main chain readjustments.

(vi) Alkali Solubility

Harris and Smith[28] followed the changes occuring on irradiation of wool in the Fadeometer by the determination of increase in solubility in 0.1N sodium hydroxide (1 hr. at 65°C) and their results show that the solubility increased from 11.9 percent for unexposed fibres to 36.2 percent for wool exposed for 100 hours. They also found a linear relationship between the decrease in percentage cystine and the increase in alkali solubility. It was also found that degree of deterioration was greater in the acid - treated fibres and somewhat less in those treated with alkali. Von Bergen's[133] experiments also show results resembling those by Harris and Smith. He found that acids increased the solubility produced by the action of sunlight on samples exposed under glass, and that while alkalis were not able to hinder breakdown of wool molecules they delayed oxidation of the sulphur. This latter conclusion was based on a stronger tin - salts reaction on alkali - treated wool, and in view of Harris and Smith figures seem rather to be due to fixation of sulphides in the fibre by alkali.

It has been shown experimentally that the alkali - solubility increased after exposure to ultra-violet light. The chemical changes which occur in wool during exposure might result in the modification of its chemical structure in any of the following ways:-

(i) The main peptide chain may be hydrolysed resulting in a reduction in mean molecular chain length,

(ii) The disulphide cross linkages may be broken by oxidation to form non-reactive side chains incapable of forming new cross linkages, or

(iii) The disulphide cross linkage may be hydrolysed.

The alkali-solubility test entails treating the fibres with a solution which will rupture the disulphide cross-links. Once this is achieved, the amount of protein which is capable of being dissolved will then depend on the extent of hydrolysis of the main-chain peptide links.

Thus the alkali solubility figure of the irradiated and unirradiated wool shows that the effect of ultra-violet irradiation could be due to the changes brought about in any one of the three ways mentioned above.

Harris and Smith[19] found that the resulting degradation of wool by ultra-violet light, determined by alkali-solubility measurements, and estimation of liberated ammonia and sulphate was directly related to decrease in the cystine content of the fibre. Although the overall rate of reaction is greatly increased by increasing the water content or the acidity, these factors do not influence the first stage in the reaction which Harris and Smith believe to be a direct activation of the disulphide bond. This probably leads to the transient formation of ions, followed by hydrolysis (which was also shown to be a photochemical process), leading to the evolution of hydrogen sulphide from the unstable sulphonic acid.

$$>CH-CH_2-S-S-CH_2-CH< \rightarrow >CH-CH_2-\overset{+}{S}+\overset{-}{S}-CH_2-CH<$$

$$\xrightarrow{H_2O} >CH-CH_2-SH + HOS-CH_2-CH<$$

The hydrogen sulphide is eventually oxidized to sulphate.

The alkali solubility increases when wool is degraded either by peptide-bond breakdown or rupture of the disulphide bonds. According to those authors moreover disorientation of the macromolecular structure, resulting from the breaking of hydrogen bonds only, also greatly increases the alkali solubility although no covalent bonds have been broken.

(vii) Urea-bisulphite solubility

There does not appear to be any reason why an increase in solubility after irradiation should not be interpreted in the same way as an increase in the alkali solution figure, namely as evidence of main chain hydrolysis.[139] A reaction takes place between the bisulphite and the disulphide cross-linkages, changing the wool molecular structure, at least in part; also urea has the power to disperse proteins, which it does by hydrogen bonding to the imidol form of the peptide link. If ultra-violet radiation attacks the disulphide bond, either directly, or indirectly, an increase in wool solubility after radiation would be expected.

The results (Figure 16) are contradictory to those obtained by Lees et al.[140] They exposed Merino 64 s (root half of staple), for seven days to radiation from a Hanovia type SNC 45-watt lamp, using a Woods glass filter at a temperature of about 25°C. The calculated percentage solubility was then less than that of undamaged wool. At the same time they recorded the high solubility of the root end of fleece wool before processing contrasted with the lower values for the whole staple in commercially scoured wool.

The present results are, however, in accordance with those of Meimaroglou[141] who attributed the causes of this discrepancy with the results of Lees to one of the following factors.

(a) The intensity of the light source

(b) The use of the Woods filter, which stops the longer wavelength of the ultra-violet spectrum but allows the shorter wavelengths to pass through.

On the basis of electron microscopic studies by Mercer[142] showing that the soluble protein comes only from the ortho-cortex and the insoluble residue consists of a mixture of para-cortex, orthocortex, cortical cell membrane and the resistant cuticle sheath, one may conclude that the action of the short wavelengths alone on the orthocortex causes a decrease in the percentage solubility.

According to Lees and Elsworth[121,140] the solubility of wool in alkaline urea-bisulphite solution decreases, to an extent depending on the conditions of pre-treatment of the fibre. The decrease in solubility is due to formation of new stable cross-linkages during alkaline treatment. Dusenbury[143] measured the cystine content and the urea-bisulphite solubilities of the 'tips' portion and found that the above values were lower than those of the 'body' of the staple. He attributed it to the indications either of the effect of sunlight and/or weathering of the fibres while on the animals, or of contact with alkaline conditions. Probably this is one of the reasons why Lees et al got the low urea-bisulphite solubility results of the tips of Merino fleece.[140]

The effect of various factors - pH value, concentration of bisulphite and of urea, temperature and time - on the solubility of wool in urea - bisulphite is quite important, and as such these factors were controlled in the experiments.

It has been observed[141] that the urea - bisulphite solubility differs between coarser and finer wools within the same top and this could be attributed to the fact that finer fibres offer a relatively larger area of attack. It is further possible that finer and coarse fibres differ in morphological structure, and that different elements of structure differ in their resistance to attack by the particular reagent, or they allow for its diffusion with greater or less ease. The above observations may well support the low values of urea-bisulphite solubility obtained in the results, assuming that the wool used is of coarse quality.

Wibanx and his colleagues[145] have pointed out that, according to electronmicroscopic studies by P. Kassenbeck, the cuticle of coarse and fine fibres differ so as to permit reagents to diffuse more easily into the finer fibres than into the coarser yarn. The high value of the urea-bisulphite solubility of the descaled unirradiated wool fibres (Table VIII) may be accounted for by the preceding suggestion.

Considering the values in Table VIII, it is noticed that after ultra-violet irradiation, the solubility of the descaled fibre is increased. The following suggestions may be put forward towards this effect. This may be due to:

(i) The formation of some cross-linkages after irradiation.

(ii) The increase in their resistance to attack by urea-bisulphite, due to change in morphological structure of the fibre whereby the diffusion proceeds with less ease.

The argument against (i) is that if cross-linkages are formed in the descaled wool there is no reason why these should not be formed in case of intact wool thereby giving decreased solubility which does not occur. (Table VIII) and Figure 16.

Further experimental work is required to be done before any definite suggestion can be put forward to account for the changes in urea-bisulphite solubility of the descaled wool fibres.

4.2 - Photochemical effect on Viscose rayon

In general, changes observed in the breaking strength and in the cuprammonium fluidity serve as a measure of degradation suffered, although the presence of other agents in the exposed samples also seem quite significant. Losses in breaking strength or work of rupture of exposed fibres indicate the extent of physical damage, while increase in the fluidity reveal the progressive molecular breakdown, or depolymerisation, that occurs in viscose rayon. Light is believed to break the molecular chains of cellulose into shorter units and to weaken the glucosidic linkages so that they are more readily attacked and ruptured by oxygen.[146] The rate of reaction is increased when moisture is present. The breakdown products obtained possess the properties of a reducing type of oxy - cellulose.[147]

When irradiated matt and bright viscose rayon fibres were immersed in 1 percent ferrous sulphate solution followed by an immersion in 1 percent potassium ferricyanide, both samples were stained deep blue while the unirradiated fibres were unstained. Also by the application of Clibbens and Geake test, the exposed viscose fibres were stained heavily dark. These tests confirmed the nature of formation of oxycellulose by the ultra-violet irradiation.

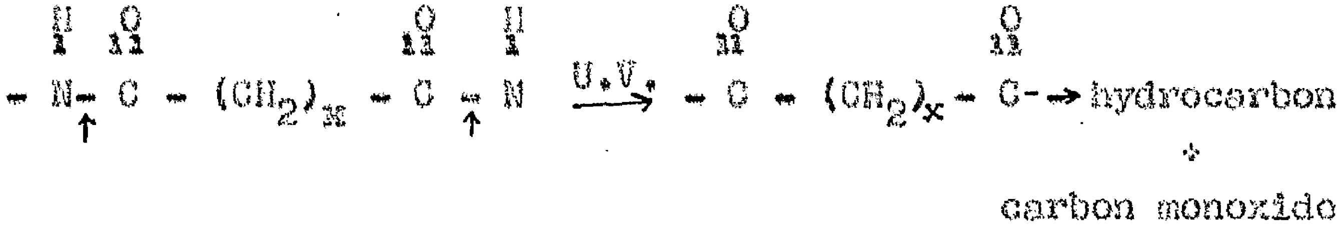
The increase in fluidity is indicative of the stepwise scission of the cellulose molecule into smaller fragments. On oxidation, the hydroxyl groups on cellulose molecules are first converted into aldehydic groups which on further oxidation are changed into carboxylic groups particularly in the case of delustred fibres where the delustring agent might prove a suitablecatalyst. The copper reduction procedure which is a measure of power of cellulose to reduce Fehling's solution to metallic copper was used to determine the presence of free aldehyde group.[148] The absence of aldehyde group was noted with both bright and matt viscose rayon suggesting that probably all the '-CHO group have been further oxidized to -COOH group in these cases after irradiation. The far ultra-violet degradation process is more rapid in action, breaking down cellulose by molecular dissociation which is independent of the presence of oxygen but in its early stages is inhibited by moisture, and causes strength losses in cotton which are accompanied by small fluidity increases.[149] It was concluded from a result of carefully conducted experiments[149] that near ultra-violet light is of insufficient energy content to cause direct molecular change in cellulose, but is able to excite the surrounding atmospheric oxygen molecules, which then attack cellulose chains.

The loss in tensile strength of the fibre after irradiation may be also due to the breakdown of cross-bonds between adjacent molecules. The tensile rupture of a viscose rayon fibre occurs mainly by the irreversible slipping of adjacent cellulose molecules over each other with the application of increasing stress the fibre elongates, at first with the reversible elasticity (the fibre structure being strained without internal slipping occuring), and then irreversibly with increasing speed until rupture takes place. Strong cross-bonds between adjacent molecules when broken by ultra-violet light might increase the possibility of internal slipping, so that the exposed fibre showed a greater irreversible extension and plasticity even at low loads.

Since the fluidity increases of samples in the present exposure test are generally not large, it is considered that measurement of the loss of strength of a material is a more sensitive indication of degradation. According to Egerton,[150] measurement of fluidity of the photochemically degraded textile fibre in a suitable solvent does not reveal the extent of degradation. For instance, viscose rayon delustured with titanium dioxide loses strength on exposure to sunlight, but the degradation is very inadequately represented by the change in fluidity of the cuprammonium solution of the viscose rayon. Schwen[68] found however, when evaluated on the basis of the deterioration of degree of polymerisation, the yarn which had not been delustred proved superior in all respects, whereas when evaluated on the basis of dry tensile strength, no difference worth mentioning could be determined on an average between delustred and lustrous rayon.

4.3 - Photochemical effect on nylon

The polymer chain is broken by the radiant energy of ultra-violet light, and the arrows indicate the probable points of cleavage. The carbonyl group of the amide linkage



$$-\overset{H}{\overset{|}{N}}\underset{\uparrow}{-}\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}\underset{\uparrow}{-}\overset{H}{\overset{|}{N}}\xrightarrow{U.V.}-\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}-\rightarrow \text{hydrocarbon} + \text{carbon monoxide}$$

absorbs energy at 2800 Å, and this energy apparently results in the scission of the bond between the imine group and the carbonyl group. This results in an decreased viscosity number after irradiation.

Nylon is a polyamide and absorption characteristics similar to polypeptides and proteins would be expected. A region of selective absorption at approximately 2300 Å has been attributed[151] to the amide group, and more particularly to the carbonyl unit of this group. The splitting of the C-N bond and removal of C = O as a result of ultra-violet exposure are possible and could be responsible for the changes in the ultra-violet spectrum.[87]

The important effect of titanium dioxide, present as a delustrant, in increasing the rate of photochemical degradation is well known. The results of work done by Egerton show however, that the titanium dioxide has little or no effect during exposure in completely dry air. Although the rate of degradation of the undyed dull nylon yarn was greater than that of the undyed bright yarn, no consistent difference was observed when the materials were dyed with very active vat dyes. There is also small effect of humidity on the rate of photochemical degradation of dyed nylon, bright or dull, and thus the effect of light on nylon seem to be purely photolytic. The light and other atmospheric conditions activate the polyamide molecule and the hydrolysis of the amide group results in new amino and carboxylic groups and also in the formation of double bonds and peroxides. This process has the general effect of reducing the viscosity of nylon in m-cresol and also reducing the tensile strength of the yarn, in addition to decreasing its molecular weight and these estimations can be a reasonable empirical basis of comparison. Since the strength of C - N bond is rather weak as compared with the C - C bond, therefore chain break probably occurs at the amide linkage.

The results of the mass spectrometric and pyrolysis tests by Achhammer et al[67] showed that the polymer molecule breaks at the - C - N - bonds in adjacent group of a molecule, the break releasing a bicarbonyl polymethylene fragment. This bicarbonyl polymethylene fragment reacts to form water, carbon monoxide, carbon dioxide, hydrocarbon and cyclopentanone, the particular products depending on the exposure conditions. The breaking of a very small proportion of the C - N bonds would result in an appreciable decrease in molecular weight and an appreciable change in physical characteristic. The experimental results show quite clearly the reduction in the molecular weight as calculated from the viscosity numbers after the increase in exposure time. Achhammer et al also found that the results of the light and electron microscopical studies suggest an increase in crystallinity particularly on exposure to ultra-violet radiant energy, though electron and X-ray diffraction failed to reveal any such change. Infra-red transmission studies of samples before and after exposure to ultra-violet radiant energy show that there are no fundamental changes in the repeating unit of chemical structure of the polyamide molecule as a result of such treatment.

Finally reference to Fig. 4 and Fig. 6 will show that there was a considerable difference between wool and Fibrolane in the relative percentage reduction in work after the two materials had been exposed to ultra-violet light. This would suggest that further examination of these materials might yield interesting information on the behaviour of protein structures.

CONCLUSIONS

CONCLUSIONS

WOOL

(a) During the initial period of exposure the effect of radiation is more severe than is the case with a later period of equal exposure.

(b) There is a loss in strength and extensibility and hence an increase in the reduction in work of rupture with exposure. Coarse yarns are less affected than finer yarns.

(c) The density and the refractive indices of the fibre increased after exposure.

(d) There is an increase in alkali solubility and urea-bisulphite solubility after exposure.

(e) The imbibition value of exposed fibres is less than that of the unexposed fibres.

(f) The specific surface area of intact wool decreased after exposure.

(g) The rate of dye absorption increased after exposure for intact wool although there was no apparent difference in the rate for exposed and unexposed descaled wool.

The radiation causes a chemical modification of wool fibre probably both in the scales and in the inner structure. The former view is supported by the work on descaled wool and the latter by the changes in density, refractive index alkali-solubility, urea-bisulphite solubility, imbibition value and change in specific surface area after irradiation. The increase in density may be due to the formation of products of hydrolysis and oxidation of disulphide bonds by action of light, thereby increasing the mass of the fibre structure. The suggestion also put forward is that under the influence of light, disulphide bonds break and the main chains may come closer to each other thus making the whole structure more compact. In addition to the breakdown of disulphide bonds, the main chains may also break and the broken chains may aline themselves near the crystallites, thus imparting an additional partial crystallinity to the exposed fibre. This suggestion is supported by the fact that the imbibition value and specific surface area of the exposed fibres are lower than the corresponding values for unexposed wool. The structural readjustment of molecular chains after exposure seems to be a good reason for these changes. The reduction in strength of wool fibre after exposure is due to the breakdown of disulphide linkages whereby there is a better chance of a slippage between the main - chains. It may be due to the cleavage of the main - chains also.

Other fibres

(a) There is a reduction in strength of viscose rayon, acrylonitrile fibres, nylon 6.6, and Fibrolane BX after exposure, suggesting that the molecular structure of these materials has been modified by the action of ultra-violet light.

(b) The results of strength tests showed that the presence of delustring agent increase the degree of fibre degradation. Thus matt M95 suffered more loss in strength than the bright M95, and matt Courtelle suffered more loss in strength than Acrilan, after exposure to ultra-violet light.

(c) The fluidity of viscose rayon increases after ultra-violet exposure, possibly suggesting a stepwise scission of the cellulose molecule into smaller fragments.

(d) The viscosity and the molecular weight of nylon 6.6 decreased after exposure which shows that polymer chain is broken by the radiant energy of ultra-violet light: since the strength of -C-N- bond is rather weak as compared with the -C-C- bonds, chain break probably occurs at the amide linkage.

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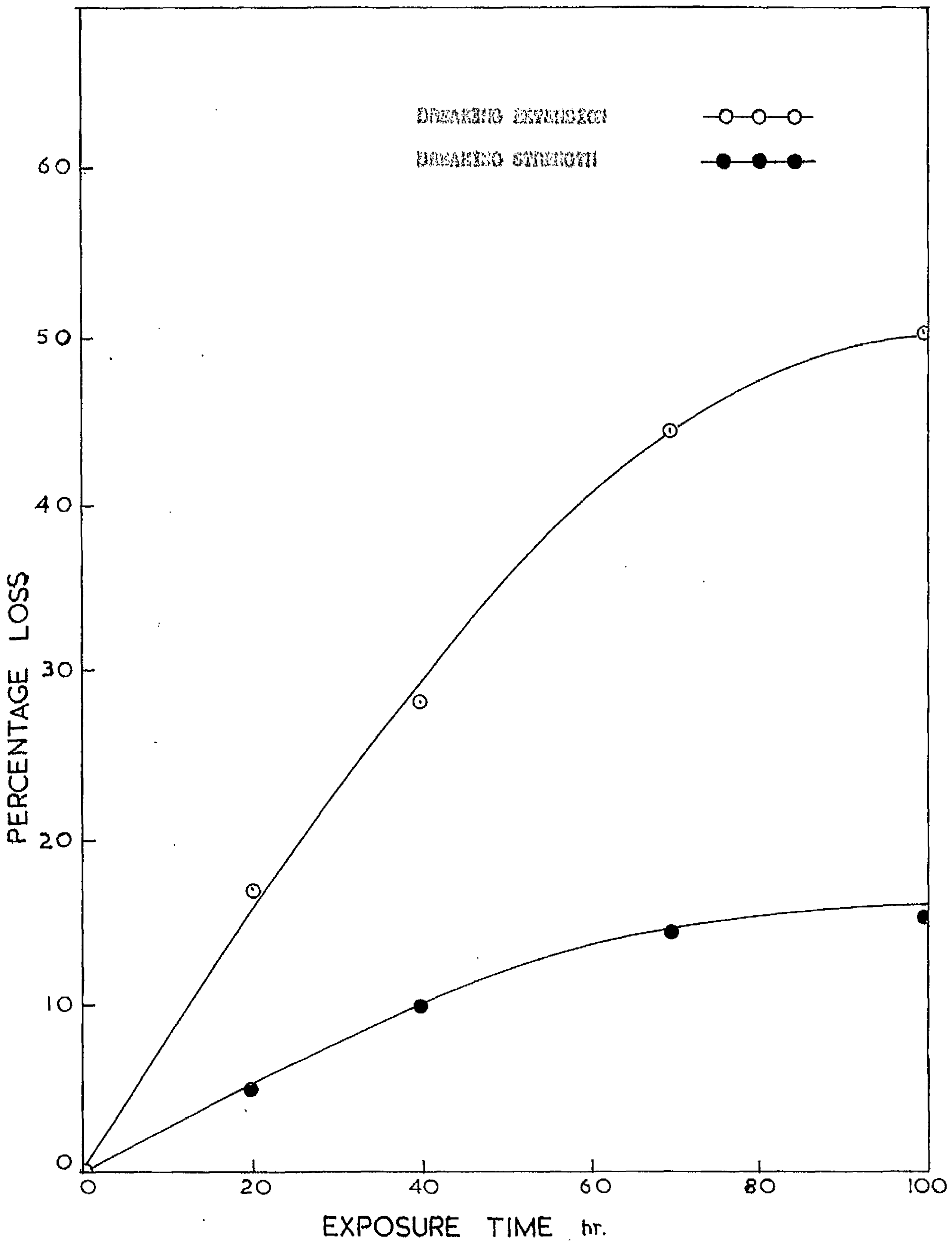

FIG. 9 - Effect of the time of Exposure on the strength and extension of a 90/1 (worsted) wool yarn

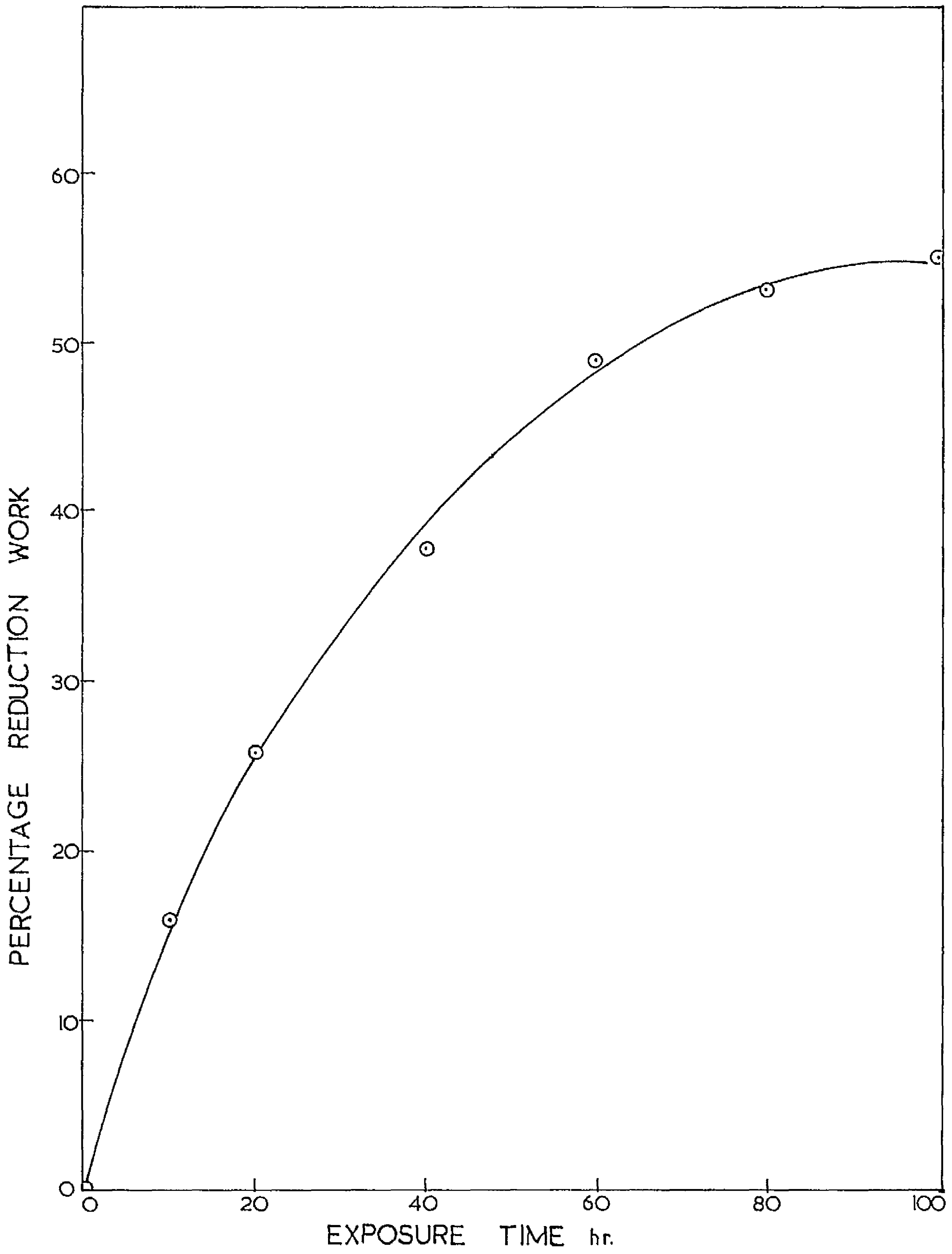

FIG. 4 - Change in percentage reduction work of wool fibre with increase in exposure time

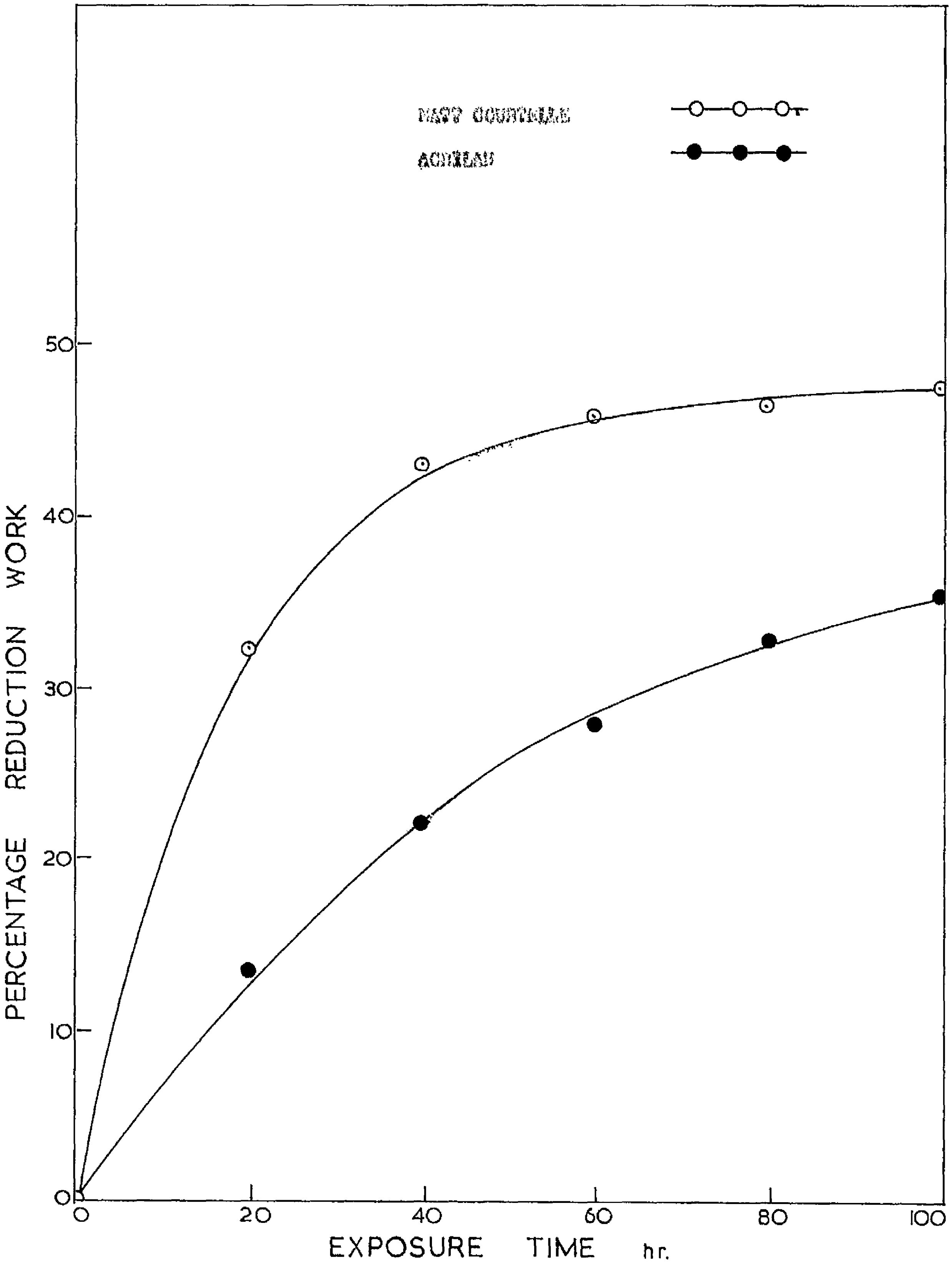

FIG. 9 - Effect of exposure time on percentage reduction work of acrylonitrile fibres

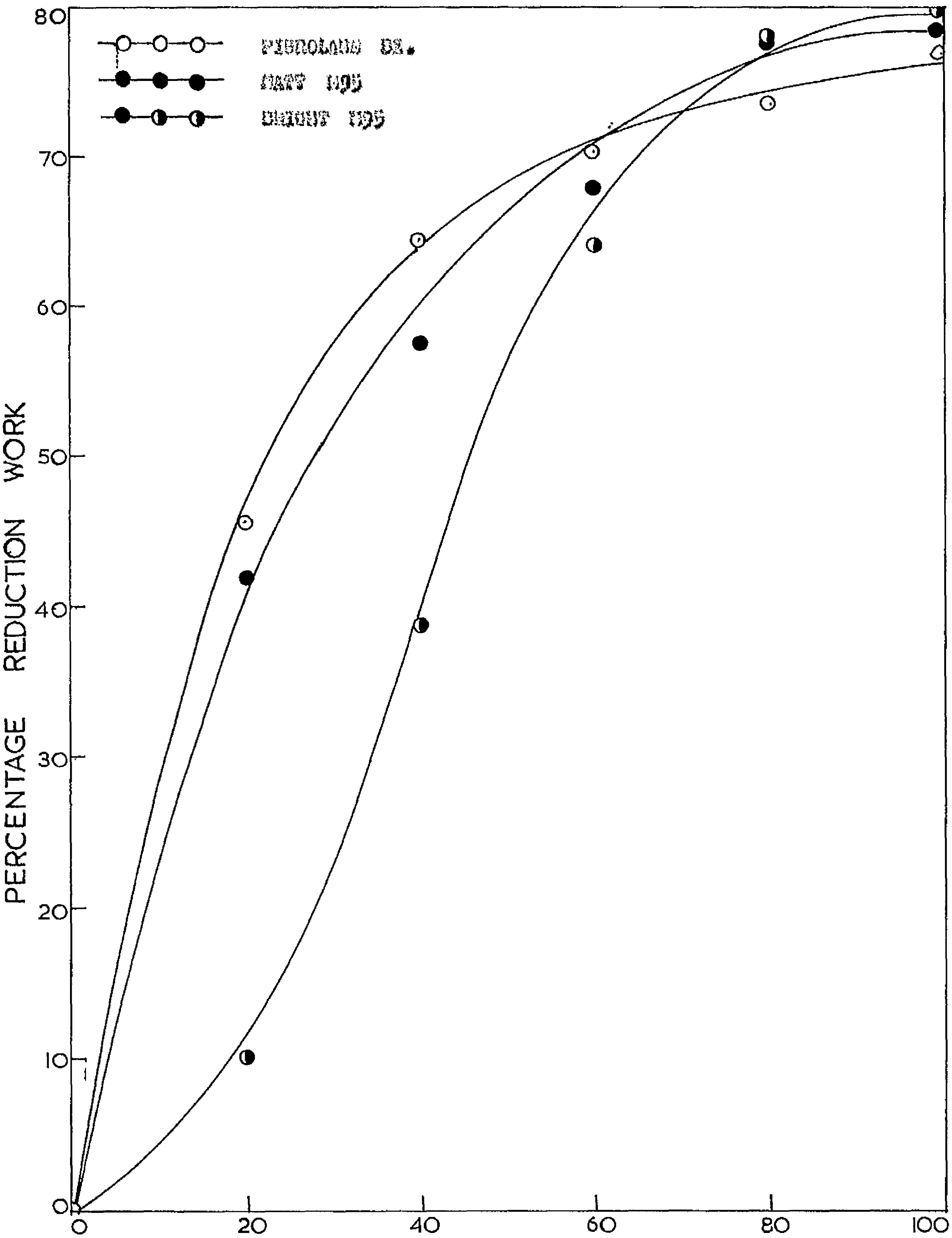

FIG. 6 - Effect of exposure time on percentage reduction work of viscose rayon and Fibrolane fibres

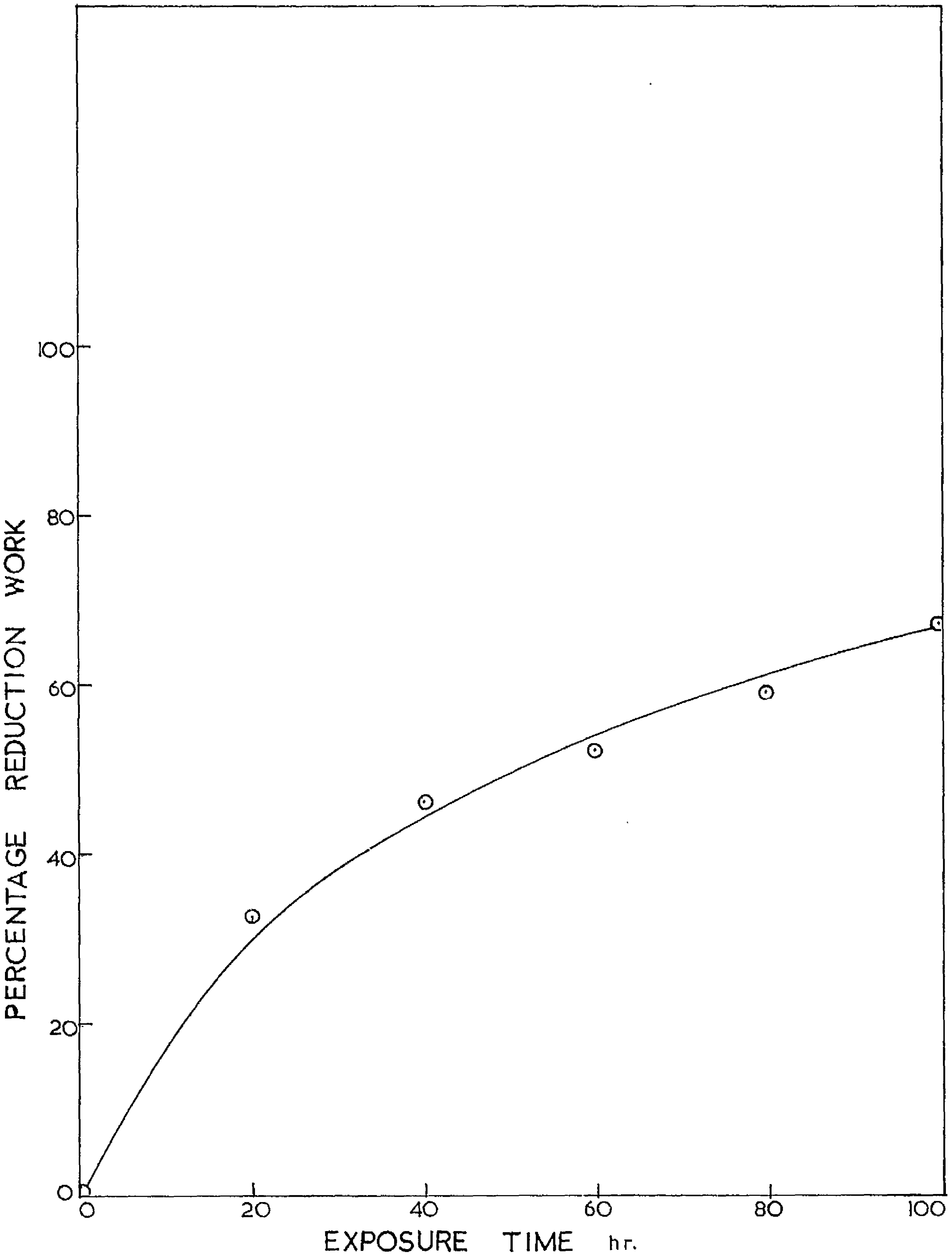

FIG. 7 - Effect of exposure time on percentage reduction work of nylon 66 (210 den.) yarn

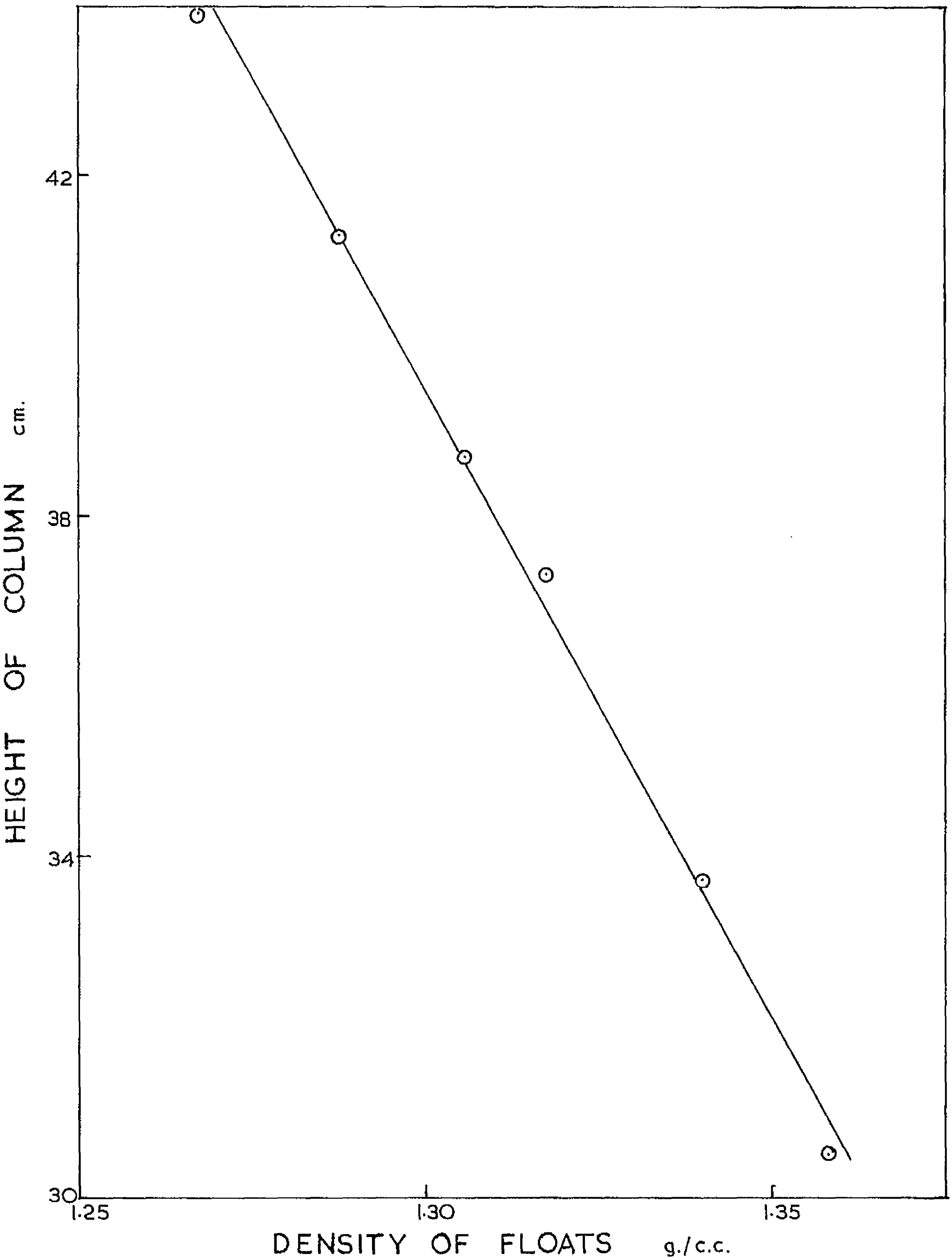

FIG. 8 - Density profile in a liquid column formed from Xylene (ρ = 0.862) to Carbon tetrachloride (ρ = 1.594)

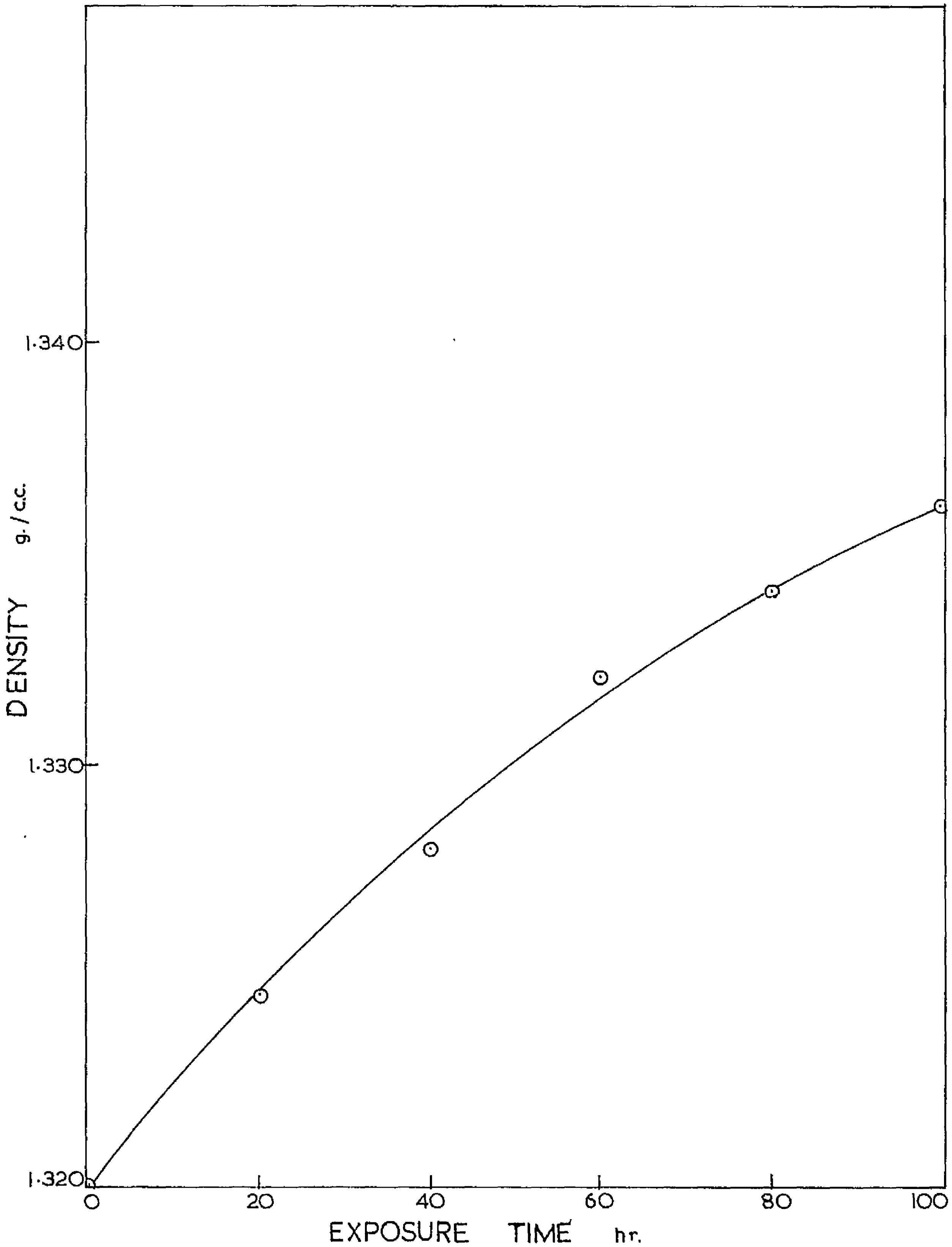

FIG. 9 - Change in density of wool with exposure to ultra-violet light

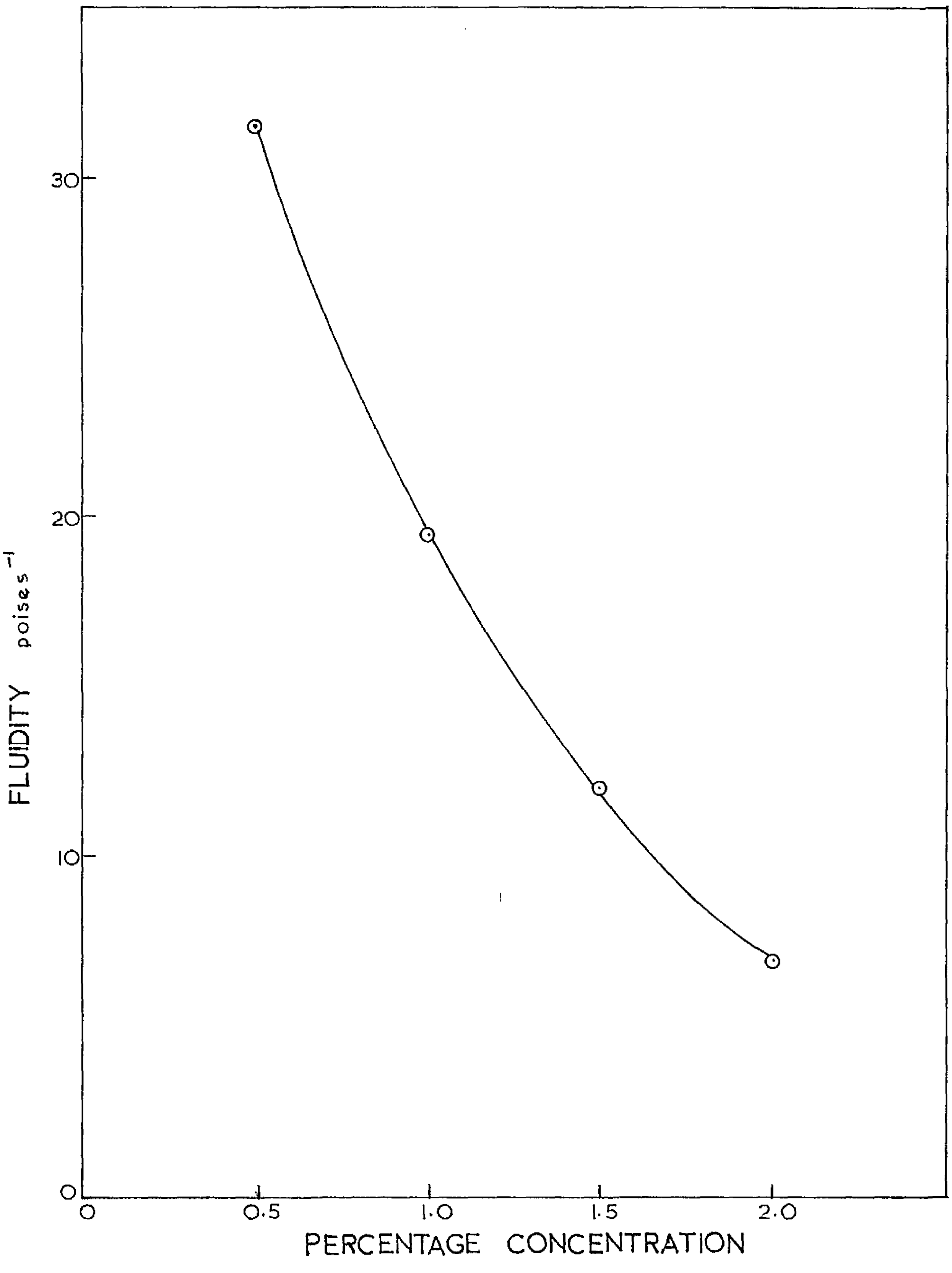

FIG. 20 - Relation between percentage concentration of viscose solution and its fluidity

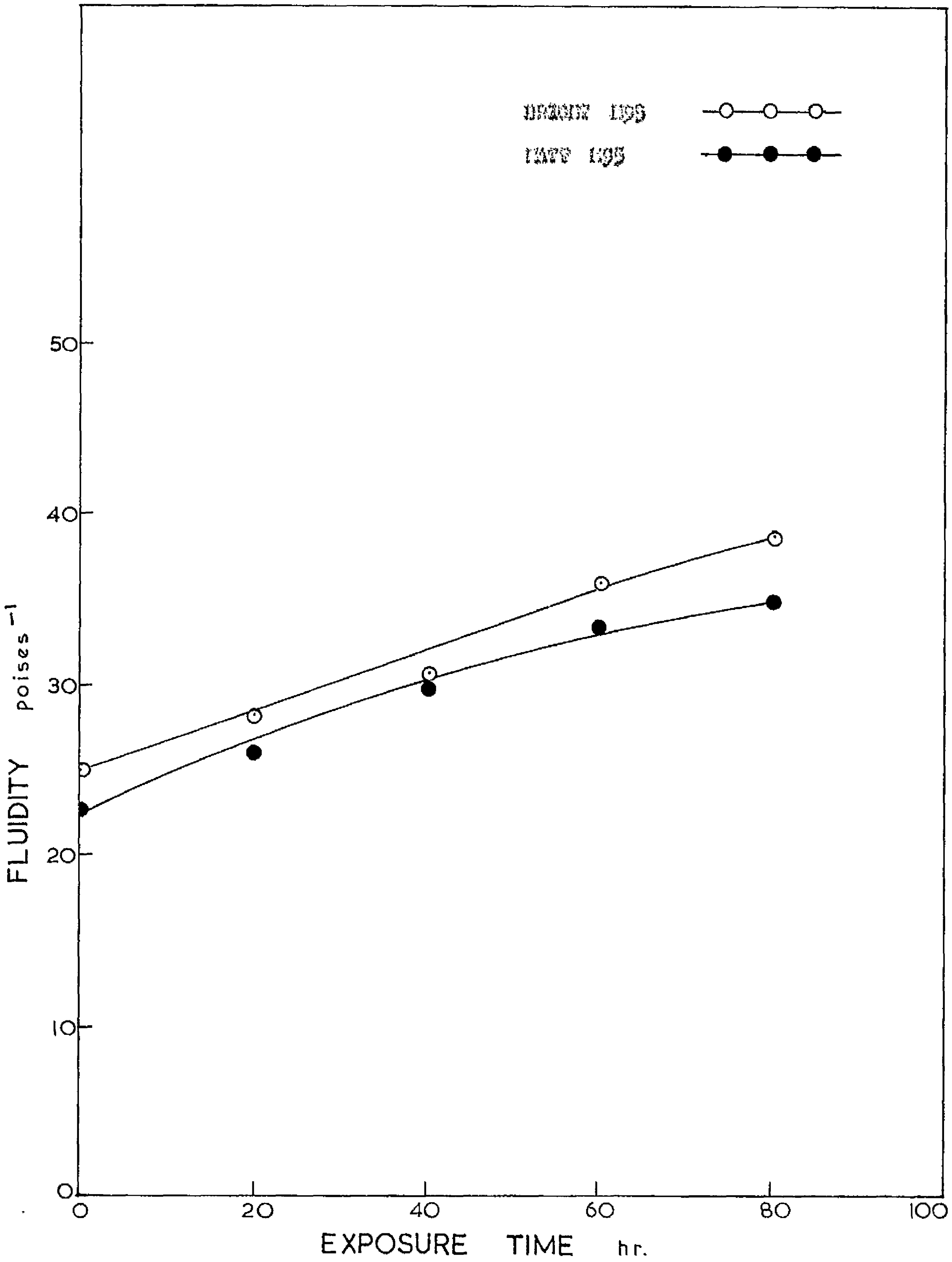

FIG. 28 - Change in the fluidity, with exposure of viscose rayon fibres

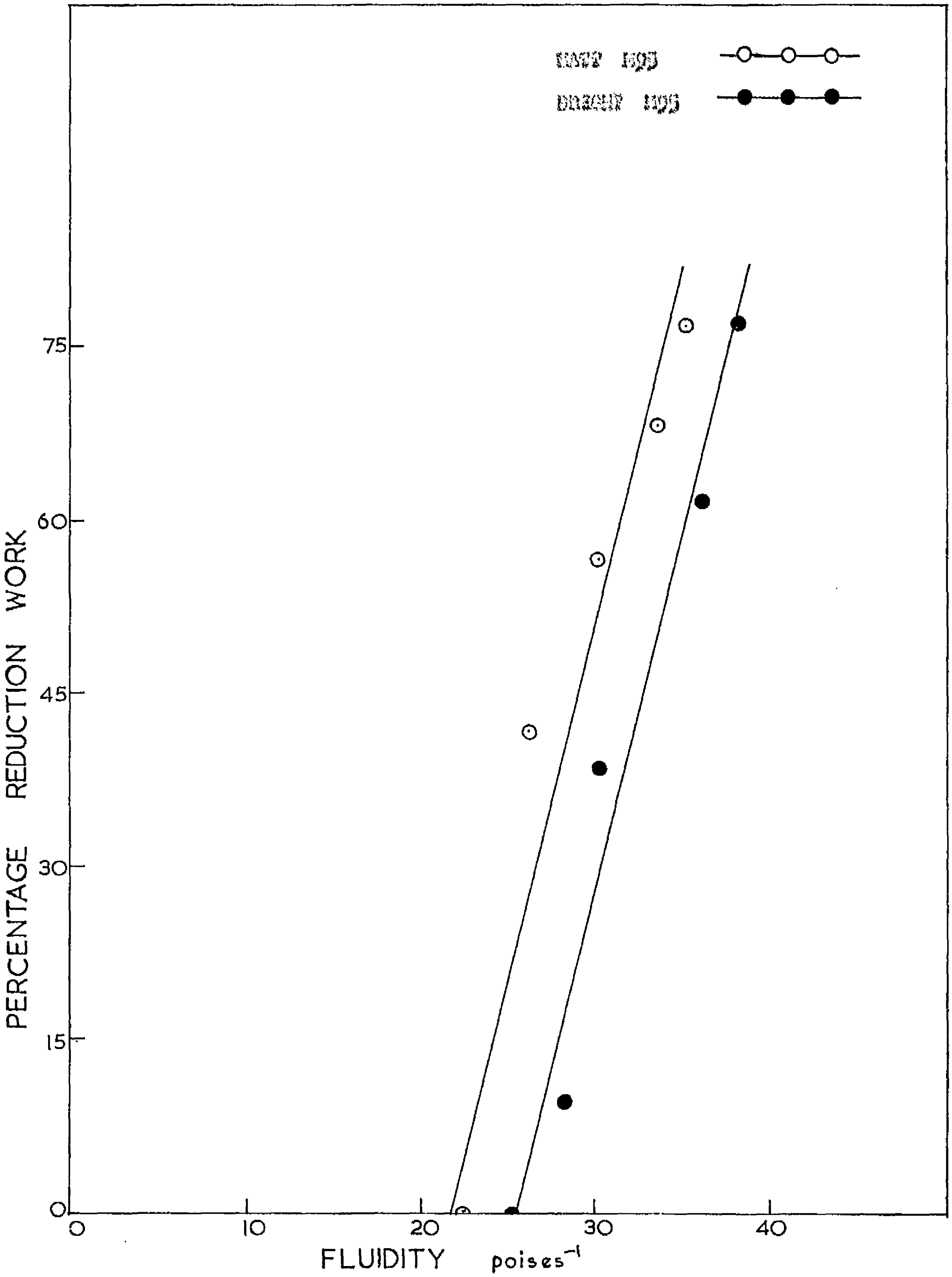

FIG.12 - Relation between percentage reduction work and the fluidity of viscose rayon exposed to ultra-violet light

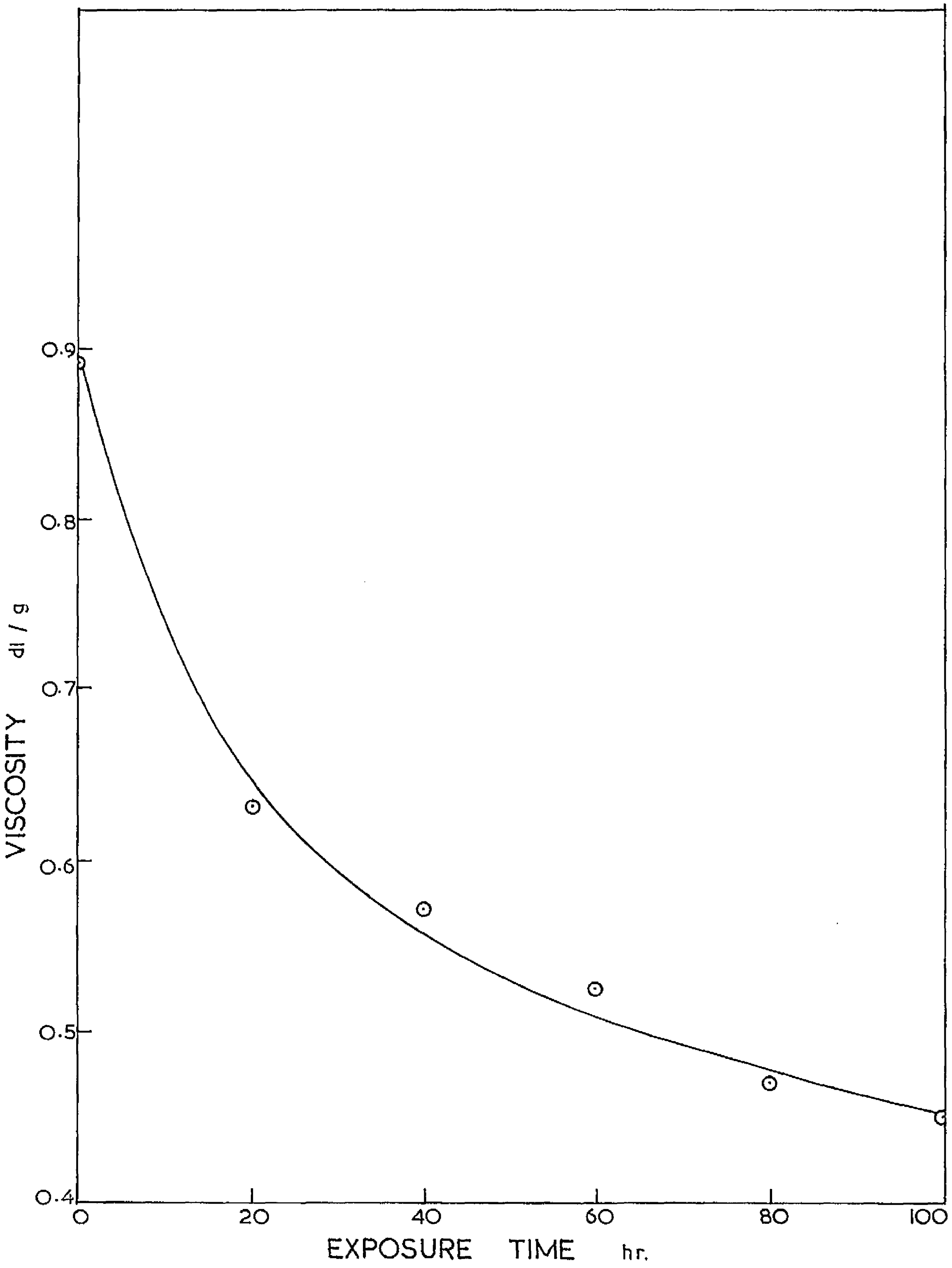

FIG. 19 - Viscosity change of nylon in m-cresol with increase in exposure time to ultra-violet light

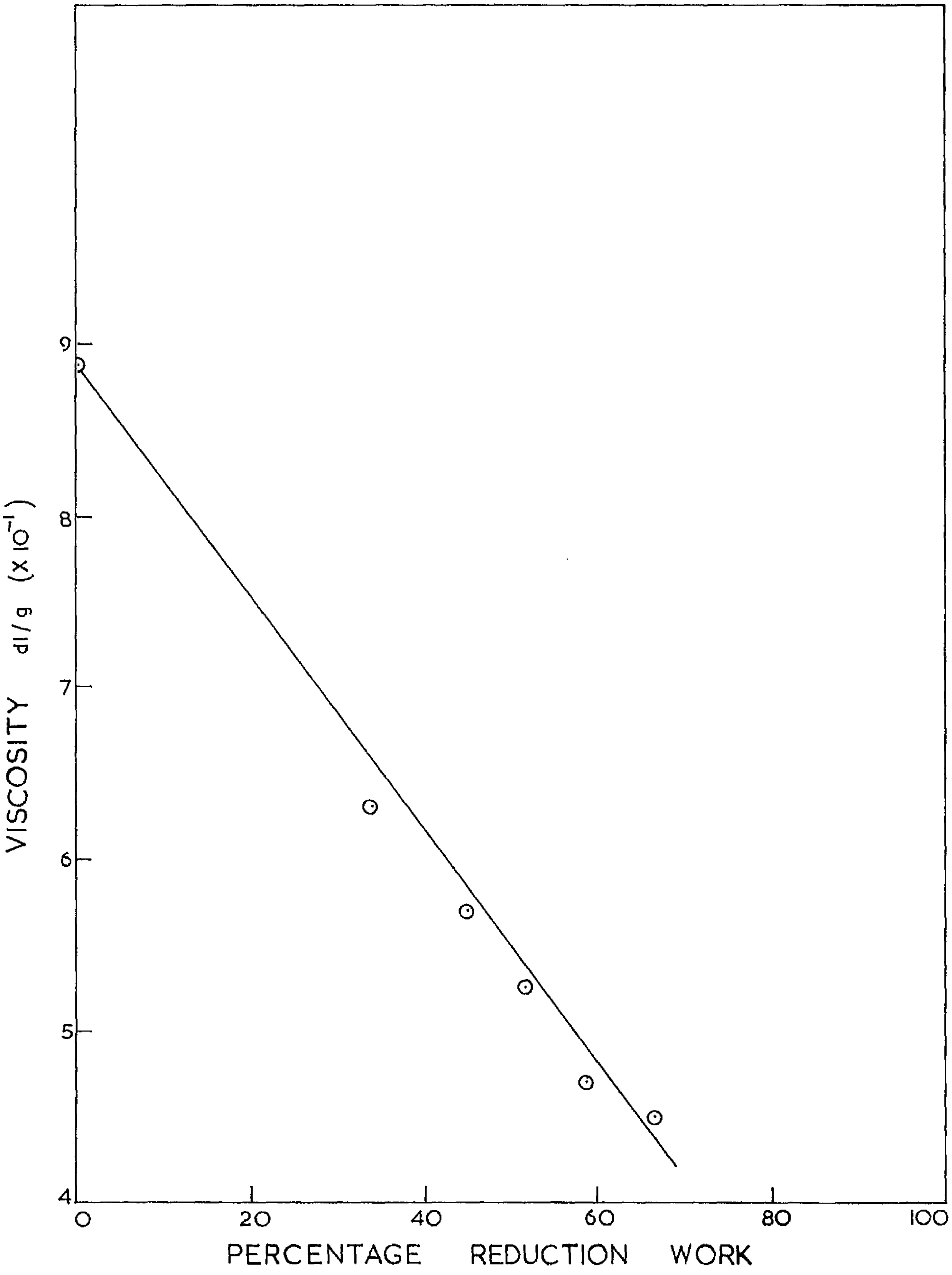

FIG.14 - Relation between percentage reduction in work and the intrinsic viscosity of nylon 66 yarn exposed ultra-violet light

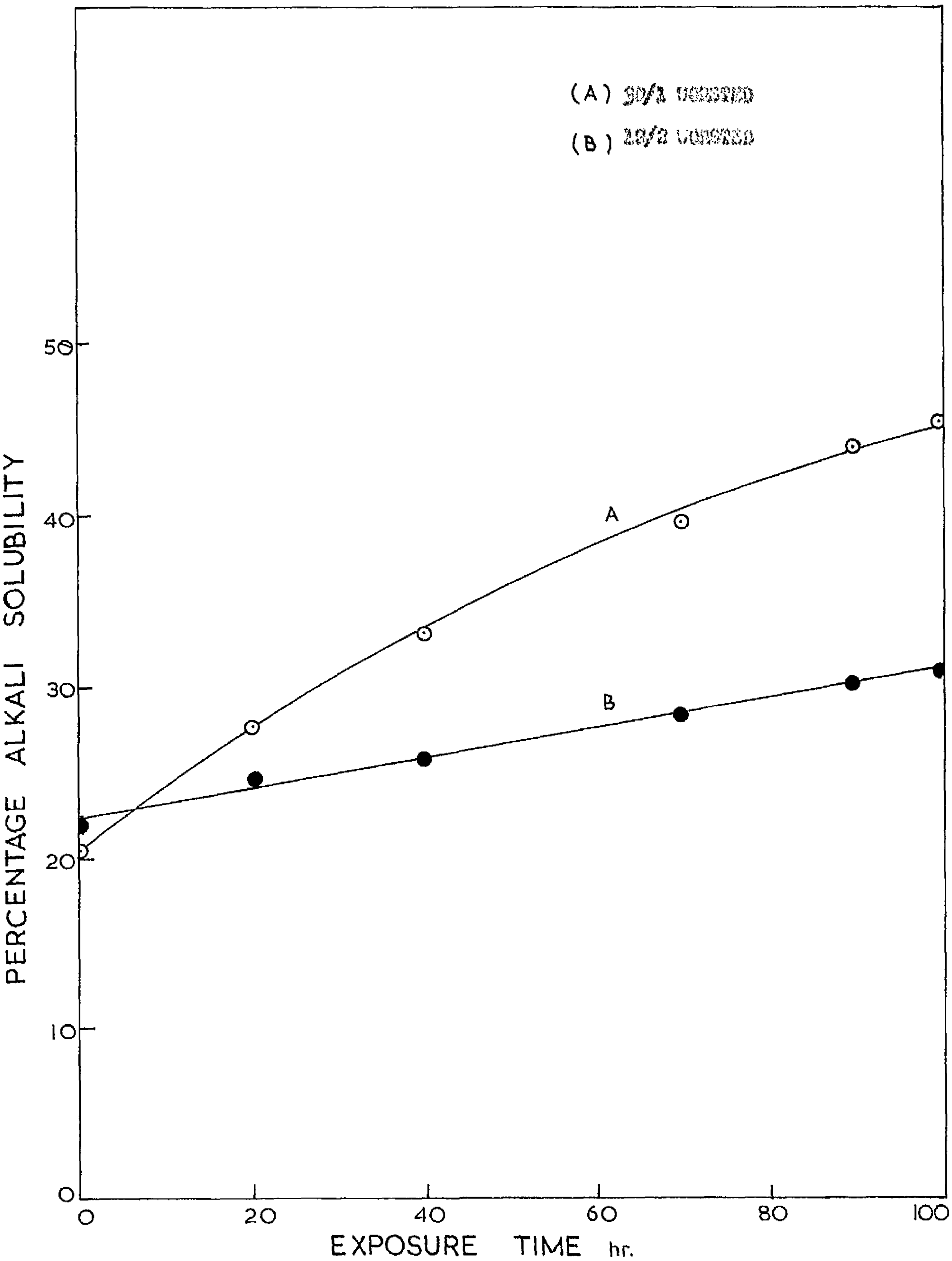

FIG. 35 - Effect of exposure time on percentage alkali solubility of wool.

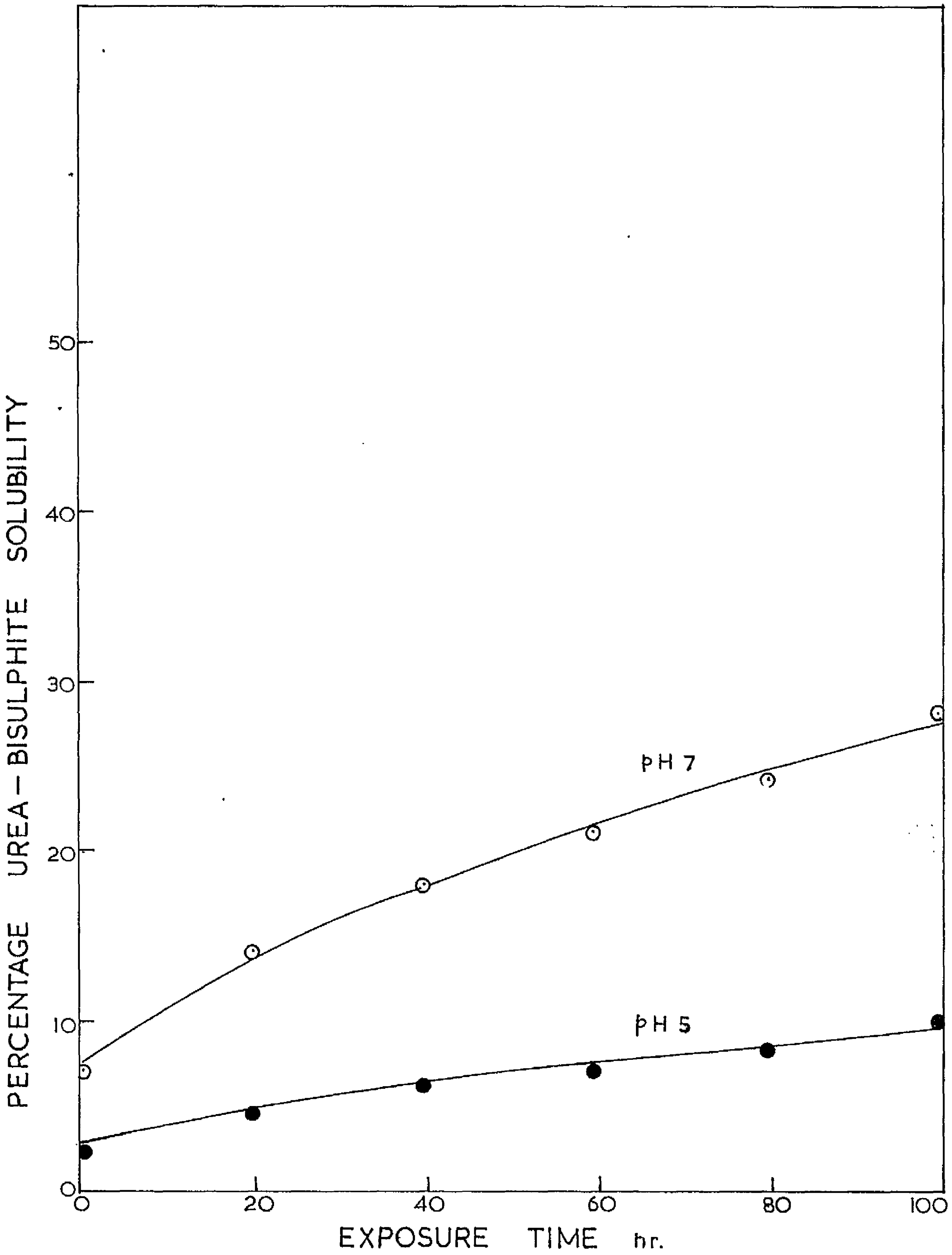

FIG.16 - Change in Urea-bisulphite solubility of wool with increase in exposure time.

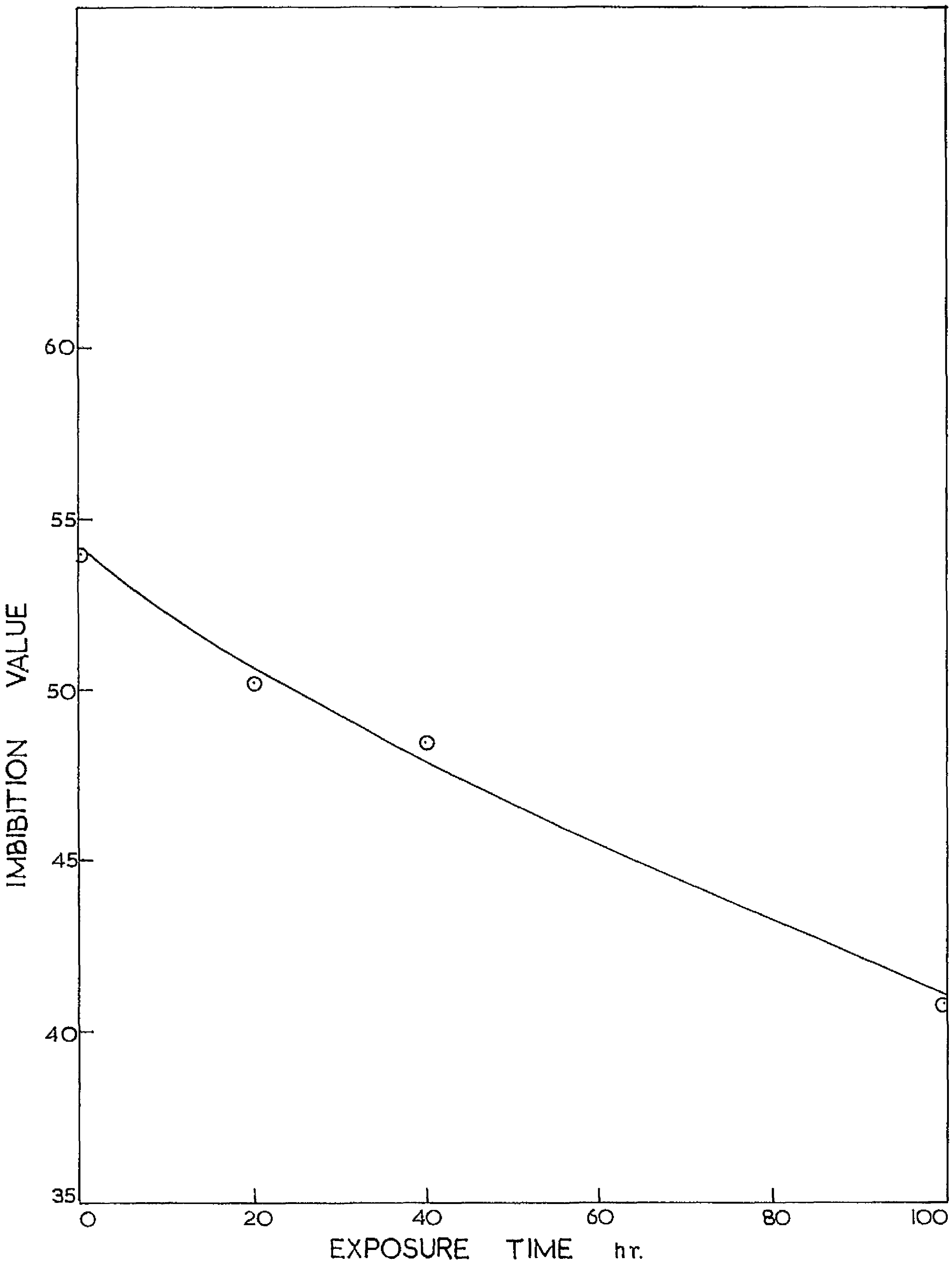

FIG.37 - Change in water imbibition value of 12/2 worsted yarn with increase in exposure time.

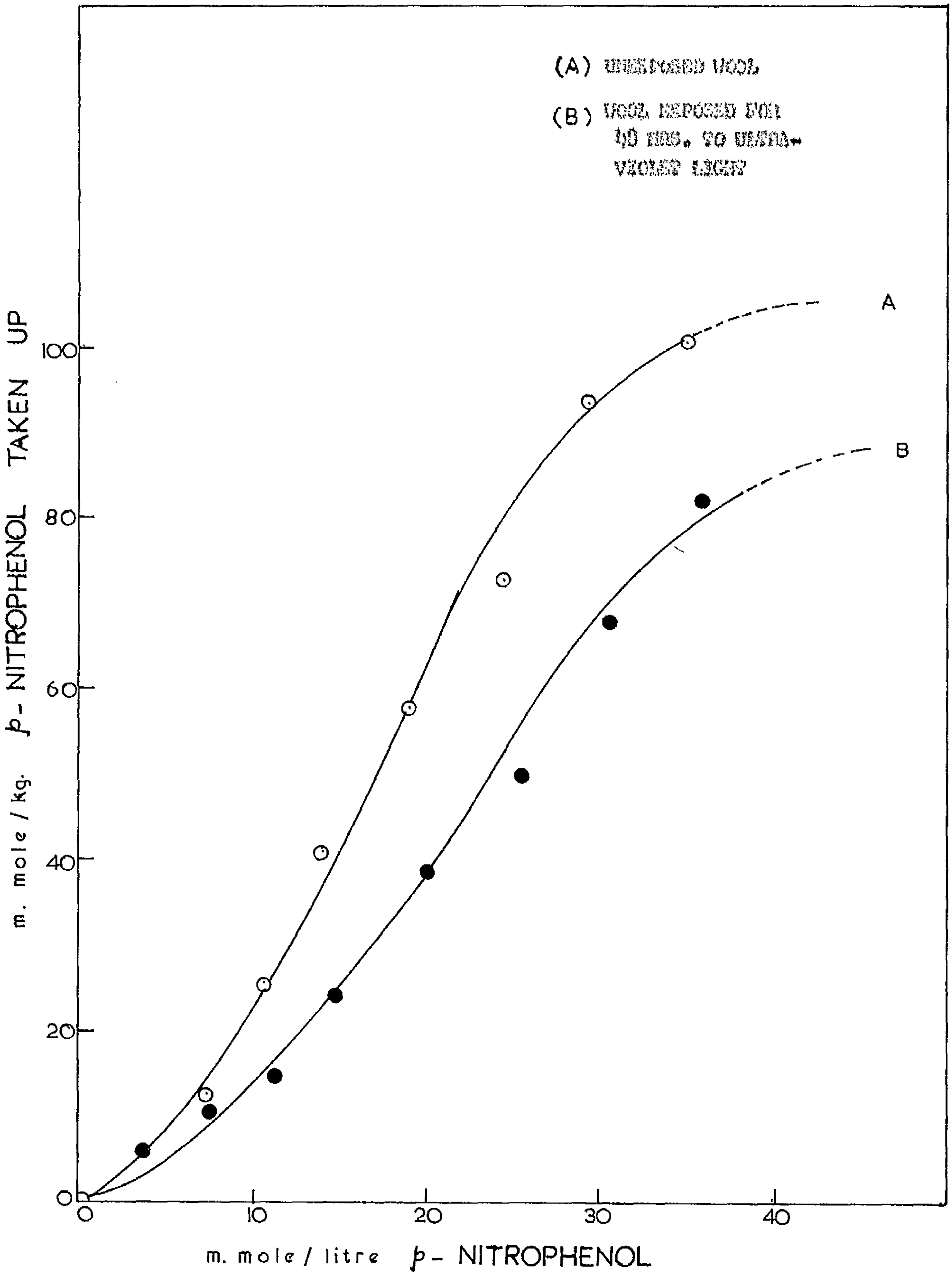

FIG.18 - Adsorption isotherm of p-nitrophenol in water (10°C) on wool.

FIG.18 - Adsorption isotherm of p-nitrophenol in water (10°C) on wool.

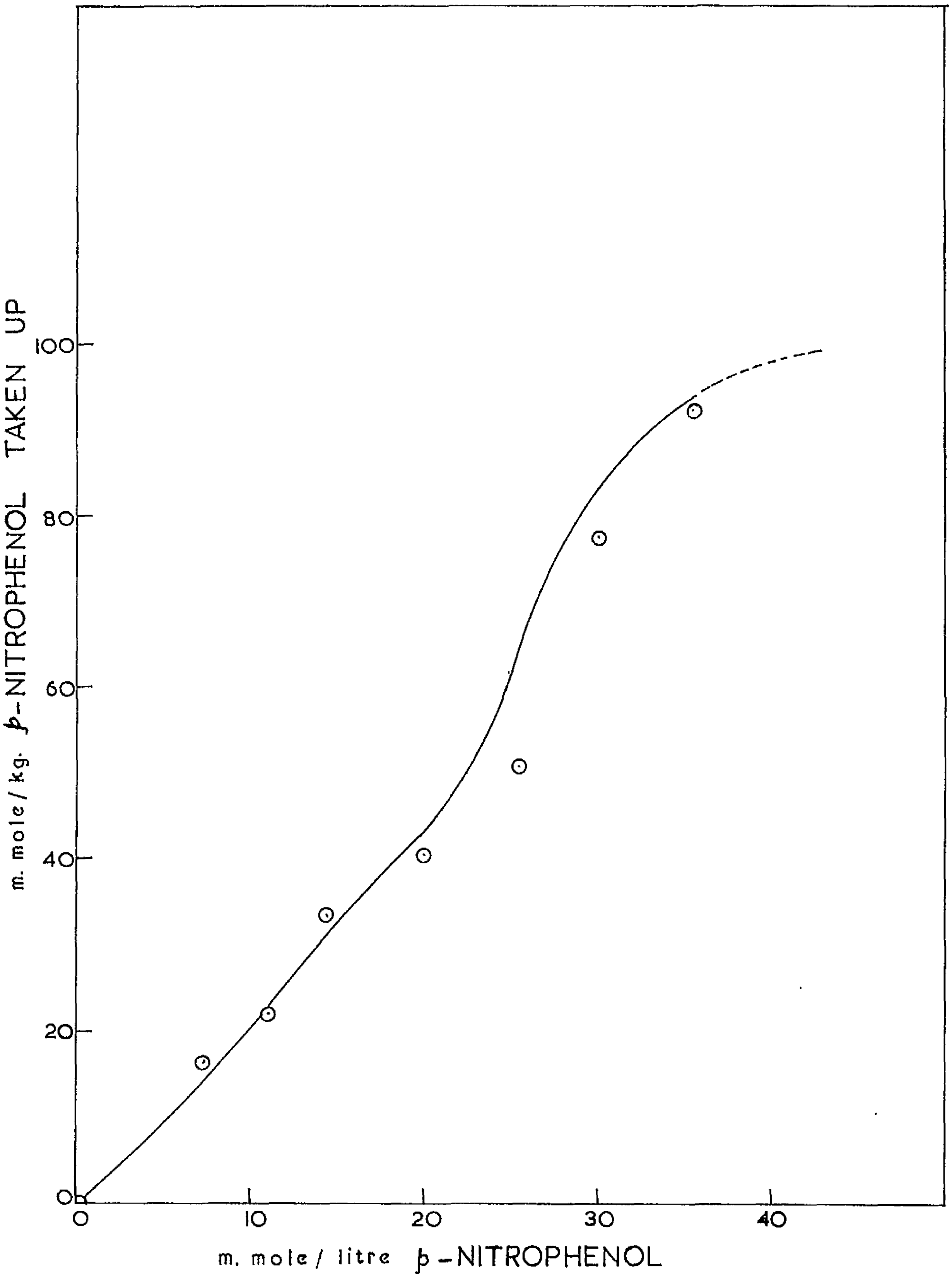

FIG. 19 - Absorption isotherm of p-nitrophenol in water (18°C) on wool exposed for 20 hours to ultra-violet light.

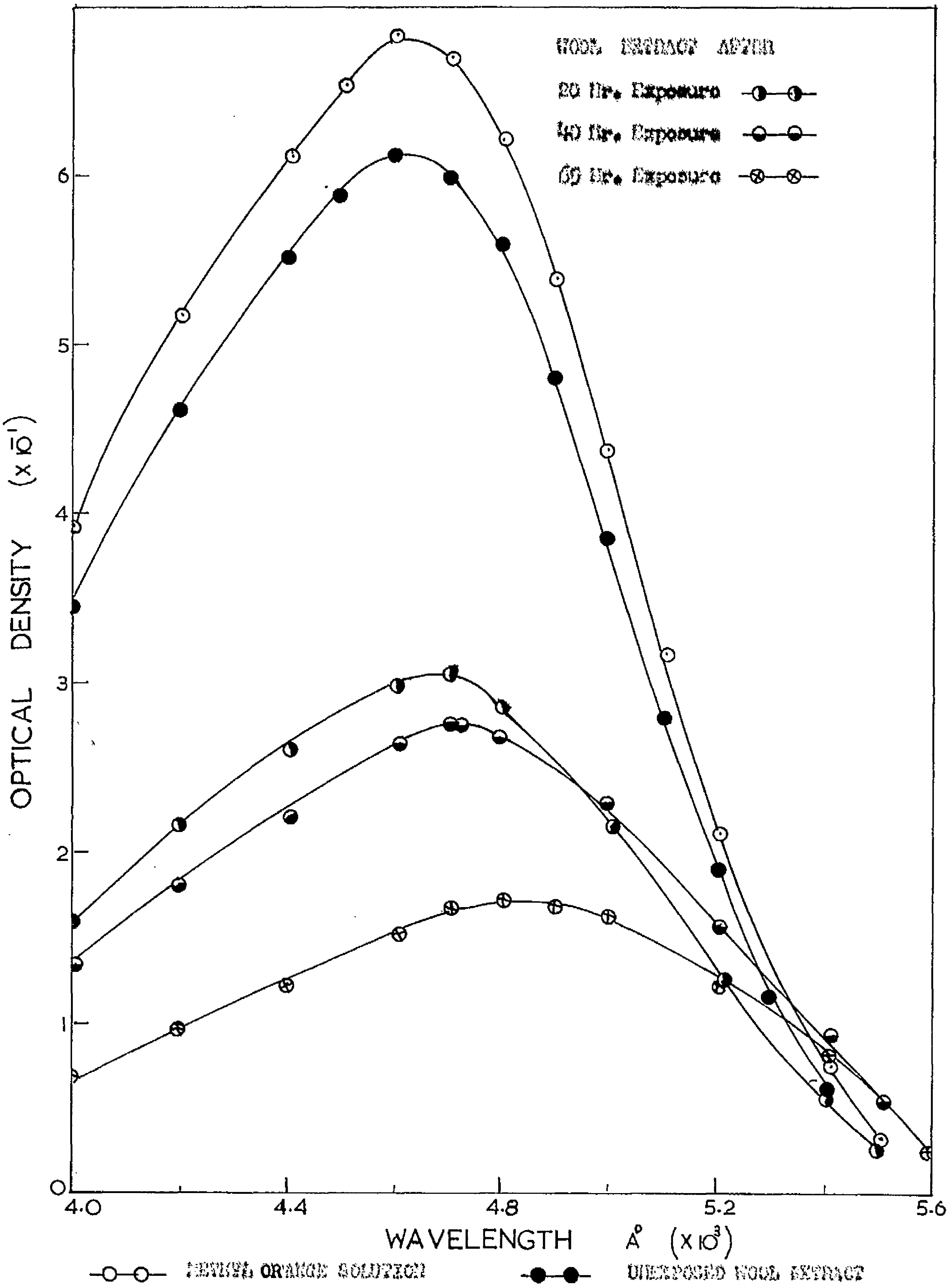

FIG.20 - Absorption spectra of methyl orange solution after 2 hr. (cold) treatment with wool, exposed to ultra-violet light.