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23 July 1969

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United Nations Industrial Development Organization

PET.SYMP. D/2

[illegible]

[illegible][1]

by

Technical Committee of Japan
Chemical Fibre Association
Tokyo, Japan

presented by

[illegible]

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1. History of development of vinylon

Vinylon is a generic name given in Japan for a synthetic fiber made from polyvinyl alcohol (hereinafter called "PVA").

PVA was discovered by Dr. W.O. Herrmann and Dr. W. Haehnel of Germany in 1924. In Germany, however, it was only made into water soluble surgical threads as it is water soluble and no further progress was made.

In 1939 in Japan, a method of making practical fibres having good hot water resistance and outstanding mechanical properties by wet spinning of PVA aqueous solution with subsequent heat treatment and acetalization was discovered. Industrial studies on this method were followed but as World War II progressed, the studies were compelled to be temporarily discontinued. After the war, the studies were resumed. In 1950 full scale production was started. Since then, production scale has been gradually expanded. In 1968 production reached 230 [illegible].

In Japan vinylon was first produced by Kurashiki Rayon Co. and Nichibo Co., and in 1963 Nihon Vinylon Co. started production, so currently there are three manufacturers.

Statistics of vinylon in countries besides Japan are not available, but North Korea, South Korea and mainland China are making full-scale production. Besides, laboratory-scale production seems to be made in France, W. Germany, U.S.S.R. and Poland.

2. Vinylon Industry today and its characteristics

Vinylon is the synthetic fiber first developed and industrialized in Japan. Japan therefore has the largest share of the world's total outputs. Growth of production and share in textile industry in Japan are shown in Table 1 and Table 2.

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United Nations Industrial Development Organization

Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries
in Developing Countries

PET. SYMP. D/[illegible]

SUMMARY

POLYVINYLALCOHOL FIBER (VINYLON) [1]

presented by

[illegible]

Technical Committee of Japan Chemical Fibres Association
Tokyo, Japan

Polyvinylalcohol fiber is produced by spinning water solutions of polyvinylalcohol, followed by heat-setting and acetalization. Polyvinylalcohol fiber, which is called vinylon as its generic name, has been developed in Japan. It is also produced in South Korea, North Korea and Mainland China.

Vinylon has a higher moisture and water absorbency than other synthetic fibers, as well as high strength and excellent resistance to chemicals and weathering. However, it has disadvantages such as a lower softening point under heat and moisture and lower elasticity. These disadvantageous properties will be improved by modification of the fiber.

Vinylon, which is produced in various filament and staple forms,

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is primarily used for industrial materials, accounting for about 65% of total vinylon used in Japan. It's primary industrial use is for ropes, fishing nets, and canvas, followed by belts, tire cords, hose and filters. Vinylon is also used for utilitary wear such as work clothes and uniforms in the apparel field. However, vinylon fine denier filament is used for high grade fabric materials with its silk like properties. In addition, vinylon of water-soluble type is used for base fabrics of chemical laces and also paper-making.

In manufacturing polyvinylalcohol, producers generally use acetylene and acetic acid through the gas-phase process to make vinyl acetate which is dissolved in methanol and polymerized, then this polymer is saponified with alkali. In recent years, however, a process of making vinyl acetate by using ethylene has been developed and production has started. Thus, the polyvinylalcohol industry has become one of important allied industries of the petrochemical industry. In Japan, the PVA industry has developed based on vinylon, and at present nearly half of production is used for other sectors than vinylon. The main uses are processing materials for textiles, films and adhesives.

Wet spinning is used mainly in manufacturing vinylon. In case of manufacturing fine denier filament, however, the dry spinning method is being employed. No particular equipment is necessary for spinning, weaving, knitting and dyeing of vinylon. All dyestuffs of direct, sulphur, vat and dispersed are applicable for vinylon. There is also a type of vinylon dyeable for acid dye.

Table 1 Output of vinylon in Japan Unit: ton

Year	Total	Staple	Filament
1956	10,718	10,688	30
57	11,731	11,601	130
58	12,552	12,501	51
59	16,563	16,253	310
60	22,693	22,140	499
61	30,002	28,799	1,203
62	35,430	34,358	1,072
63	37,376	35,668	1,708
64	44,170	41,028	3,142
65	49,056	44,919	4,137
66	54,108	48,342	5,766
67	60,620	54,318	6,302
68	69,152	62,528	6,624

Table 2 Output Textile in Japan (1968)

		Output, (ton)	Ratio, (%)	
Synthetic fibers	Nylon	21[illegible],007	31.3	
	Polyester	181,[illegible]	26.5	
	Acrylic	159,530	23.3	
	Vinylon	69,152	10.1	
	Polypropylene	31,731	4.6	
	Polyethylene	11,9[illegible]2	1.7	
	Polyvinyl chloride	9,818	1.4	
	Vinylidene	5,6[illegible]3	0.8	
	Others	1,526	0.2	
	Total	6[illegible]5,3[illegible]8	100.0	33.4
	Rayon staple	366,550		17.9
	Rayon filament	142,284		6.9
	Cotton yarn	551,182		26.9
	Wool yarn	163,748		8.0
	Bast fibre yarn	117,798		5.8
	Silk yarn	23,120		1.1
	Grand Total	2,050,380		100.0

Characteristics of vinylon industry are as follows:

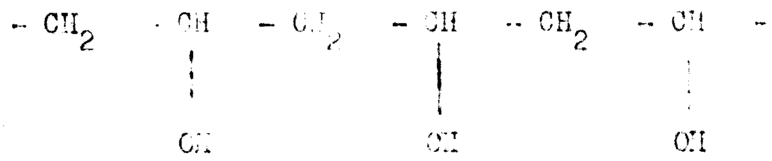
(1) In material supplies: Both acetylene and ethylene can be major raw materials for vinylon. Acetylene is readily obtainable from carbide or natural gas and ethylene from petroleum. The acetylene made from carbide was used as raw material at first, then acetylene made from natural gas was used. Today, ethylene produced in petrochemical industry is also used. Other raw materials besides the above major raw material include acetic acid, methanol, formalin, sulfuric acid, and Glauber's salt which are readily accessible chemicals. Most of them will become available at a lower price with progress in the petrochemical industry.

(2) In processing: Processing of synthetic fibers such as spinning, weaving, knitting and dyeing usually require highly advanced techniques but vinylon can be satisfactorily processed [illegible] rayon [illegible] processing equipment with slight modifications. In addition, vinylon produces less static charge making process control easier. [illegible], too, special equipment such as for polyester or polypropylene is not required.

(3) In markets: Vinylon finds wide range of uses as will be mentioned in later paragraphs. Above all, it has a firm market in such essential applications as industrial materials and utility clothing. On the other hand, soluble fibers and silk-like fibers utilizing the speciality of vinylon have extended unique applications. Its special characteristics include excellent adhesion to rubber, outstanding weather resistance and low static charge while its general properties resemble those of rubber.

3. Chemical Structure

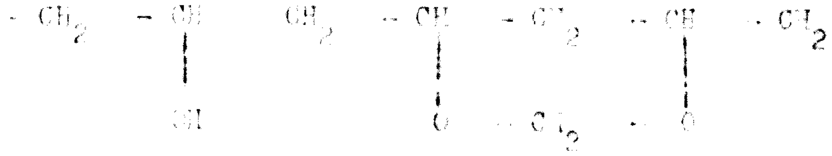
Basic chemical structure of vinylon is as follows:



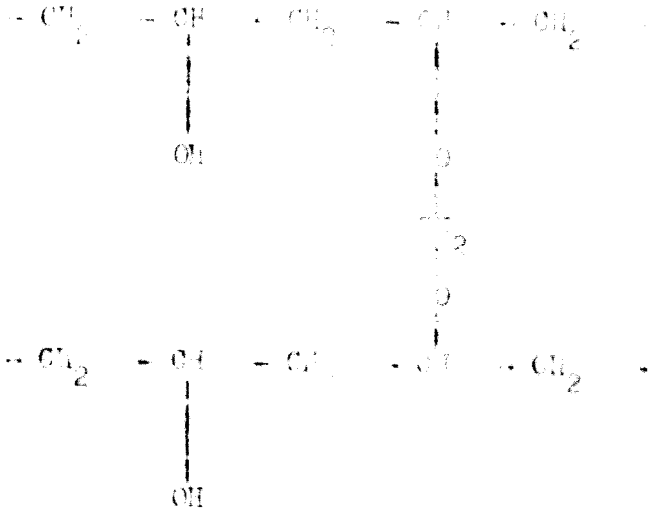
$$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-$$

Since a fiber like this is soluble, it cannot be directly used as textile fiber, but can be used in special applications. An example of such uses is found in fiber as binder in paper making where adhesion [illegible] water [illegible] heat are utilized. [illegible] in [illegible] use with other fibers to make [illegible] [illegible] by dissolving away this fiber [illegible] are as the same of the for chemical lace.

In case of [illegible] fiber, [illegible] PVA fiber is heat treated it is further reacted with formalin. The chemical structure of the formalinated molecule is as follows:

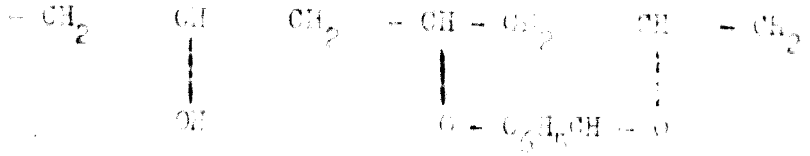


Mostly reaction occurs within the molecular chain, but some cross linking seems to take place between the chains depending on reaction conditions. Such cross linking can be shown by the following.



PVA has a number of highly reactive hydroxyl groups. Theoretically, the degree of etherisation is calculated to reach 87.7 mol %, but industrially, the degree of etherisation is kept within 30 mol % because heat treatment forms fine crystals resulting in reduction of highly reactive hydroxyl groups in the heat treated PVA fiber.

In lieu of formalin, other aldehydes are sometimes used. An example is the use of benzaldehyde for the purpose of enhancing vinylon's elasticity. Its chemical structure is as follows:



$$-CH_2-\underset{OH}{CH}-CH_2-CH-CH_2-CH-CH_2$$
$$O-C_6H_5CH-O$$

In another example, the raw material PVA is amino-etherized before spinning to fiber in order to improve dyeability with acid dyes on the fiber.

4. Types and Properties

4.1. Types of Vinylon

Vinylon is produced in various forms including staple, tow and filament, which are used in wide applications. Main types and applications are listed in Table 3.

Table 3 Main Types and Applications of Vinylon

Type		Denier	Main Applications	Remarks
Normal	Staple	1 - 2	Clothing Furnishing Industrial filter cloth	100% vinylon spun yarn, cotton blended spun yarn Rayon blended spun yarn
		2 - 12	Clothing Furnishing	Rayon blended spun yarn Wool blended spun yarn, other synthetic fiber blended spun yarn

[illegible]		[illegible]	[illegible]	Remarks
[illegible]	[illegible]	[illegible]	[illegible]	[illegible] filaments, [illegible] [illegible] blended [illegible]
	[illegible]	[illegible]	[illegible]	[illegible] filaments
		[illegible]	[illegible]	[illegible] ity filaments
Special	St[illegible]	[illegible]	[illegible]	[illegible] fibre as binder
	[illegible]	[illegible]	[illegible]	[illegible] filament
	[illegible]	[illegible]	[illegible]	[illegible] etc.

[illegible].2. [illegible]

[illegible] many outstanding [illegible] relatively low specific gravity, [illegible] than [illegible] resistance, bending [illegible] bility and good [illegible] properties under dry heat. [illegible] chemicals, [illegible] softening point [illegible] heat setting pro- perties [illegible] softening point

under wet heat is [illegible], it is higher than 100°C, which will not be obstructive in practical use. Also its elasticity can be measurably enhanced through reaction with benzaldehyde. Lack of heat setting properties can be compensated through permanent pressing by the use of the chemical reactivity of hydroxyl OH groups.
The general properties of vinylon are summed up in Table [illegible].

Table [illegible] Properties of Vinylon

		Staple		Filament	
		Normal	High tenacity	Normal	High tenacity
Tensile strength, (g/d)	standard	[illegible]	[illegible]	[illegible]	[illegible]
	wet	3.2-5.2	5.3-6.[illegible]	[illegible]-[illegible].2	[illegible]-[illegible]
Dry-wet strength ratio, (%)		7[illegible] - [illegible]5	78 - [illegible]	[illegible]	[illegible]
Loop strength, (g/d)		[illegible].2-5.2	[illegible]-5.[illegible]	[illegible].5-6.0	[illegible]-1[illegible].0
Knot strength, (g/d)		2.[illegible]-[illegible].0	[illegible]-[illegible].2	2.[illegible]-[illegible]	[illegible]7-[illegible].0
Elongation, (%)	standard	1[illegible] - 2[illegible]	1[illegible] - 17	17 - [illegible]	[illegible] - 22
	wet	1[illegible] - 2[illegible]	13 - 17	17 - 2[illegible]	10 - 26
Elastic recovery (%)	3% elongation	70 - 85	7[illegible] - [illegible]5	70 - 90	70 - 90
Initial Modulus, (g/d)		25 - 70	7[illegible] - 10[illegible]	60 - [illegible]	70 - 180
Apparent Young's modulus (kg/mm²)		3[illegible]-[illegible]00	[illegible]0-12[illegible]	700-[illegible]50	[illegible]00-2000
Specific gravity		1.26 - 1.30			
Moisture Regain (%)	Official			5.0	
	standard conditions 20°C 65% RH	[illegible]5-5.0		3.5-[illegible].5	3.0-5.0
	20°C [illegible]% RH	1.2 - 1.8			
	20°C [illegible]% RH	10.0 -12.0			
Effect of heat and state of incineration		Softening point: 220 - 230°C Melting point: Indefinite Burns slowly while softening and shrinking. Turns into brown or black irregular fragile lumps.			

Other properties are:

(i) Fatigue resistance: Vinylon's abrasion strength, bending strength and impact strength are all better than those of cotton.

(ii) Chemical resistance: Vinylon is resistant to acids, alkalis, organic solvents, oils and many other chemicals. However, it swells or dissolves in hot pyridine, phenol, cresol, conc. hydrochloric acid, conc. sulfuric acid, conc. nitric acid and formic acids.

(iii) Weathering resistance: Vinylon is so outstanding in weathering resistance that it causes little change in strength, elongation and little discoloration despite long exposure to sunlight. Especially vinylon without treatment with formaldehyde has superior weathering resistance.

(iv) Corrosion resistance: Vinylon is extremely resistant to and virtually unaffected by bacteria, insects and mildew.

(v) Dyeability: Vinylon is dyed fairly well with various dyestuff. In applications requiring bright color, the filaments made from partially amino-etherized PVA by dry spinning process are used. Where especially high color fastness is required, solution-dyed fibers are produced.

5. Applications

Vinylon finds the largest outlet in industrial use for its toughness and durability. In Japan, approximately 65 % goes to industrial use. However, it also has widespread uses in utility clothing such as working wear and student's wear. Its moderate hygroscopic property makes it suitable for underwear. For silklike feeling and luster, vinylon filaments for high quality clothing have also been developed.

5.1. Clothing

Vinylon is used in clothing for its advantages - strength, durability, soft feeling, moderate hygroscopicity, warmth retention and economical advantage of all synthetic fibers. However, its uses are concentrated in the fields of utility clothing such as student's wear, working wear, and knitted goods because of a slight deficiency in its elasticity.

(1) **Working** Wear, Porter's Wear and White Garments. Most common are blends of 50% vinylon and 50% cotton. Working clothing of 100% vinylon is also used where special chemicals are handled. Vinylon's share in the total textile consumption for working wear is approximately 30%.

(2) Uniforms & [illegible] of formaldehyde treated vinylon with improved dyeability are used for uniforms including student's wear and business wear. Vinylon accounts for approximately 10% of the fibres used in this area.

(3) Nightwear and Bedding. For nightwear, vinylon is used in pyjamas, negligees and other similar products with a unique handle. It is blended with rayon, polyester etc. Bedding includes sheets, covers for the bedding and quilt covers.

(4) Sports Wear. With the advantages of its high absorption property, abrasion resistance and ease of handling, vinylon is widely used in sporting goods and shirts. Vinylon is also best suited for making "judo" wear. Vinylon has taken [illegible] of this market.

(5) Knitted goods. Knitted goods of 100% vinylon are used for winter wear and blended with 50% [illegible] for other garments. Use [illegible] in blends with wool and other fibres is also increasing.

(6) High Quality Clothing. Filaments from vinylon are used as 100% vinylon or blended with polyester and other synthetic fibers, in high quality clothing such as kimono fabrics, women's wear fabrics, suit linings, scarfs, and neckties because of their better dyeability and silkly lustre and feel.

5.2. Furnishings

Because of high strength, durability, abrasion resistance and weathering resistance, vinylon has been recently used in furnishing such as curtains, carpets, table clothes and upholsteries.

5.3. Industrial Uses

With advantages of its high strength and resistance to heat, weatherin corrosion and chemicals, vinylon is voluminously used for industrial purposes.

(1) Fishery

(i) Fishing Nets: Vinylon is largely used in fishing nets for its property advantages -- high tensile and impact strength, non-corrosiveness, weathering resistance and ease of handling. Yarn commonly used is 20's spun yarn and 250 - 1000-den filament yarn. Other types [illegible] lines and fixed nets. Vinylon's share in the total fishing net consumption is about 15%. Vinylon is also used in laver nets as it promotes build-up and growth of spores. It represents 20% of the total synthetic fibers used for this purpose. For laver nets, 500-den monofilaments are often used.

(ii) Ropes: Combining strength with corrosion and weathering resistance, vinylon is finding use in ropes for fishing, land and marine and other general purposes. [illegible] in the [illegible] hemp, jute and cotton are used. Yarn used is spun yarn of [illegible], 5's and [illegible] and filament yarns of 1500, 2000 and [illegible] den. Vinylon represents about 15% of the total rope consumption.

(iii) Long-lines: Vinylon's outstanding strength, durability and ease of handling make it useful in long lines for fishing tuna in place of cotton. Vinylon has a large share in this market. Spun yarn of 20's is used for main lines and filament yarn of 1000, 1500 and 2000 den for branch lines.

(2) Building and Construction

(i) Belts: Vinylon is making major inroads in conveyor belts with advantages of its high strength, impact strength, resistance to bending fatigue, heat resistance, water resistance and adhesion to rubber. For this purpose spun yarn of [illegible]'S and 10'S as well as monofilament yarn of 1200 denier are often used. Some belts use 100% vinylon while others use vinylon in the [illegible]. Vinylon has taken about [illegible] of the [illegible] consumption.

(ii) Hoses: Spun yarn of 10'S and 20'S and filament yarn of [illegible] 2000 [illegible] used in the braided hoses. For fire hoses, [illegible] spun yarn is used as warp only, [illegible] filament yarn [illegible]. Vinylon accounts for approximately [illegible] of the total fiber consumption for hoses.

(iii) Sheets: Vinylon can be easily finished for waterproof and possesses high strength, [illegible] resistance and weathering resistance. Because of these properties and its [illegible] advantages, vinylon is [illegible] used as sheets for building and construction purposes. [illegible] of these applications are [illegible], and [illegible]. [illegible] vinylon [illegible] durability, especially [illegible] water and [illegible] ports and harbors, where vinylon sheets and [illegible] used. Vinylon's share in these applications is [illegible].

(3) Transportation.

(i) Tire Cord: [illegible] vinylon is [illegible] used for small-sized tires because its strength, [illegible] resistance, adhesion to rubber and [illegible] are better than those of cotton and rayon. The yarn [illegible] spun yarn of 20'S and 22'S [illegible] filament yarn of [illegible]. Consumption of vinylon in bicycle tire cords is as high as [illegible].

(ii) Sheets, Covers and tents: Owing to its superior property combination, vinylon is extensively used in sheets for land transportation such as truck sheets, cover and tarpaulin [illegible] tents, boat covers, coach [illegible] and wagon sheets. Other applications include storehouse tents and camp tents. Recently use as car covers is also increasing. Yarn used is spun yarn of 10 - 60'S and filament yarn of 70 - 1200 denier. Vinylon is used in about [illegible]% of the applications in this field.

(4) Agricultural and Forestry

(i) [illegible] the fiber vinylon can be used without [illegible] over a long period of time even when exposed to [illegible] or buried underground, vinylon [illegible] is used for agricultural and horticultural purposes. Spun yarn is mainly used. Where shading is especially required, [illegible] yarn is used. Vinylon's share in the [illegible] Cloth is [illegible] 75%.

(ii) Protective nets [illegible] Vinylon's resistance to sunlight and ease of handling are utilized in making protective nets against birds. [illegible] filament of 300 denier is mainly used for this purpose.

(5) Packing and [illegible] Materials

Vinylon is [illegible] tough, light and rotproof, finding use as fertilizer bags, mail bags, cereal bags and vegetable bags. Yarn mainly used is spun yarn of 16 - 30'S.

(6) Sewing Thread

Vinylon is mainly used in sewing threads for general industrial materials, [illegible], shoes, and working wear. Besides spun yarn of 5 - 30'S, filament yarn of 250 - 1200 denier is often used.

(7) Filter Cloth

With advantages of its high strength, durability, chemical resistance, non-corrosiveness and economical advantages, vinylon is used in filter cloth for food, chemicals, ceramics and metal industries. Yarn used is spun yarn of 20'S or filament yarn of 250, 500 and 1000 denier. Consumption of vinylon represents 20% of the total filter cloth.

(8) F.R.P. (Fiber reinforced plastics)

Taking advantage of the high Young's modulus, excellent impact strength, heat stability, and chemical resistance, cloth made mainly from high-tenacity 1200-den filaments or cut fibers of 1 - 15 mm are used as reinforcing fibers for various thermosetting resins.

(9) Special Applications (Soluble Vinylon)

(i) Paper Making Binders: Fibrous binders cut in 3 - [illegible] mm do not dissolve in water of normal temperature but [illegible] in hot water. Paper can be manufactured by using the conventional paper making machine. These binders melt to bind in the dryer part and are therefore [illegible] used in [illegible]. [illegible] they are particularly useful for making rayon or synthetic fiber papers.

(ii) Chemical Lace Ground Cloths: Silk which has so far been used must be dissolved by alkali, but vinylon dissolves in hot water. This [illegible] soluble vinylon filament yarn of [illegible] - 100 denier widely used in this field. Other applications include the use of soluble vinylon as [illegible] materials for spinning, weaving and knitting.

6. Polyvinyl Alcohol

Direct raw material of vinylon is PVA. PVA is produced from acetylene or ethylene by way of vinyl acetate (VAc). A process of synthesizing from ethylene was announced by [illegible] in [illegible]. Since then, it has been intensively studied in many countries. Since further reduction in the price of ethylene is anticipated with the tendency to construct larger plants, the trend in the future is toward increasing the employment of the ethylene process in place of the acetylene process.

6.1. Manufacturing process of PVA

This process can be generally classified into [illegible] processes of 1) synthesizing of vinyl acetate (VAc) through reaction of acetylene with acetic acid or ethylene with acetic acid and oxygen;

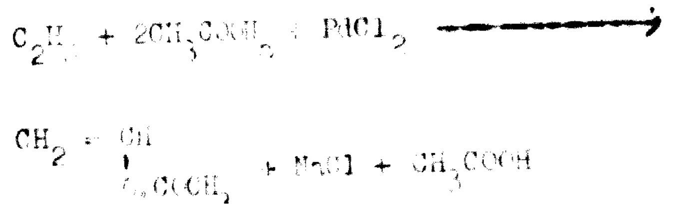
2) polymerization; 3) saponifiaction and 4) recovery of saponified waste solution. Acetic acid is discharged in the form of ester, acetate or sodium acetate as will be mentioned later. If acetic acid is recovered for reuse, PVA will be obtained from acetylene and water or ethylene and oxygen, with acetic acid being just recycled.

(1) Synthesis of VAc: There are liquid-phase and vapor-phase processes for synthesizing VAc from acetylene and acetic acid, but industrially, the vapor-phase process is mostly used. In the vapor-phase process, acetic acid vapor and acetylene are allowed to pass through zinc acetate on activated carbon as catalyst to react at a constant temperature.

$$C_2H_2 + CH_3COOH \rightarrow CH_2 = CH.O.COCH_3$$

Since the reacted liquid contains 40 - 60% of acetic acid and a small quantity of by-products - impurities, it is distilled to yield refined VAc. The separated acetic acid is reused. In the method of synthesizing VAc from ethylene, liquid-phase process and vapor-phase process have now been established as industrial methods. In the liquid-phase process, a palladium salt and the acetic acid salt of an alkali metal are dissolved in acetic acid and by blowing ethylene through it VAc is produced.

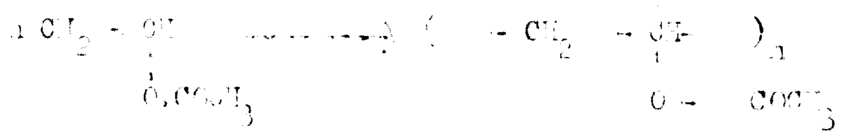
Typical example is:



$$C_2H_4 + 2CH_3COONa + PdCl_2 \longrightarrow CH_2 = \underset{OCOCH_3}{\underset{|}{CH}} + NaCl + CH_3COOH$$

The Pd formed here does not act as a catalyst and therefore reoxydation of the Pd is necessary. For this purpose, benzoquinone, or a copper salt, iron salt and oxygen are added to the system as oxydizing agents for the Pd. In general, the liquid-phase process is understood to use a Pd salt. In the vapor-phase process a method of using metal Pd as a catalyst is mainly used. An advantage of the vapor-phase process lies in excellent yield of VAc. On the other hand, it has drawbacks in the rather high capital cost and the difficulty of removing the heat of reaction.

(2) Polymerization of VAc: Polymerization of VAc is a process of turning VAc into PVAc.



$$n\,CH_2 = \underset{OCOCH_3}{CH} \longrightarrow (-CH_2-\underset{O-COCH_3}{CH}-)_n$$

At present almost solution polymerization is employed mainly for the polymerization process of PVAc for textile purposes. The solvent normally used is methanol [illegible] benzol [illegible] possible is common [illegible]. The polymerization amount of catalyst [illegible], amount of solvent and polymerization temperature [illegible] to prevent the degree of polymerization [illegible] molecular weight distribution of the PVAc.

(3) Saponification of PVAc: [illegible] carried out either by alkali [illegible] or acid [illegible] used for PVA [illegible] caustic soda and sodium [illegible]. The saponification reaction [illegible]:

PVAc [illegible] ...... (1)

PVAc + H [illegible] ...... (2)

AcO [illegible] ...... (3)

In complete absence of water, only the ester conversion reaction of the formula (1) occurs. In the presence of water and methanol, only the direct saponification reaction of the formula (2) takes place. Industrially, [illegible] methanol [illegible] used and therefore the reaction [illegible] in the form given in formula (1) and only [illegible] formulas (2) and (3). This means that the amount of caustic soda used can be less than one-several tenth the equivalent.

(4) Recovery of Saponified Waste: Saponified waste solution contains methanol, methyl acetate and sodium acetate. These ingredients are separated through distillation. Methanol is reused, and methyl acetate is hydrolyzed into acetic acid and methanol which are both recovered. Sodium acetate is commonly turned to acetic acid and Glauber's salt by addition of sulfuric acid to recover acetic acid.

6.2. Non-Fiber[1/] Applications of PVA

In Japan, major emphasis in study on PVA has been put on the raw material for vinylon and in this manner PVA has been industrialized. Some works, however, have dealt with the development of applications in areas other than vinylon, considering PVA as special water soluble high molecular weight compound. Such applications have shown steady growth. This growth is being accelerated by increased production of PVA and reduced production cost. Thus various property advantages of PVA have come to be used in a wide range of applications. Growth of demands by applications in Japan is shown in Table 5.

Table 5 Growth of demands of PVA by Applications

Unit: ton

	For vinylon	For non fiber use (1)	Total (2)	(1)/(2)%
1955	5,900	1,100	7,000	16
1968	72,100	68,200	140,300	48

In non-fiber applications, greater portion of PVA goes to finishing of textiles as well as films and sheets. The rest is used in paper finishing or as emulsion stabilizers and adhesives. Each application is as follows:

[1/] Non-fiber applications mean other than for vinylon fiber production

(1) Textile Finishing: The major use in the field are in warp sizing for weaving PVA is often used with starch. It has been shown to increase the strength of the warp covering yarn and gives excellent effect in stabilising size solution. Most is used for synthetic fiber spun yarn, some for cotton and rayon spun yarn and others for filaments. Other applications include hand finishing of fabrics, binder paste and finishing resin with thermosetting resins.

(2) Films and Sheets: Because of moisture permeability, high clarity, and gas barrier properties, PVA films are used for packaging textile products and food. PVA films are also used as mold release films. PVA sheets are used as belts for textile machinery for its resistance to oil. PVA treated with formaldehyde-polyvinyl-formal has water absorption properties, this is being used for sponge cloths.

(3) Paper Finishing: In paper finishing, PVA is used for surface sizing of kraft liners or printing paper in order to improve surface strength and printability. Some of these are used in clay coating of high quality paper thus replacing the conventional casein.

(4) Emulsion Stabilizer: PVA is often used as emulsion stabilizer for VAc emulsions because it has protective colloid properties. It is also used in suspension polymerization of vinylchloride.

(5) Adhesives: PVA finds extensive use in adhesives for kraft bands, in bag making and for paper lamination. It is also used as remoistenable adhesives for gummed tapes and postage stamps or as plywood adhesives in combination with urea resins. Other applications include binders for plaster board, ferrite and fiberboard, protective film for metals, glass, cabinets and plastics, and refrigerants. In these applications, PVA of proper degree of saponification and degrees of polymerisation is used. PVA is rarely directly used for making Vinylon.

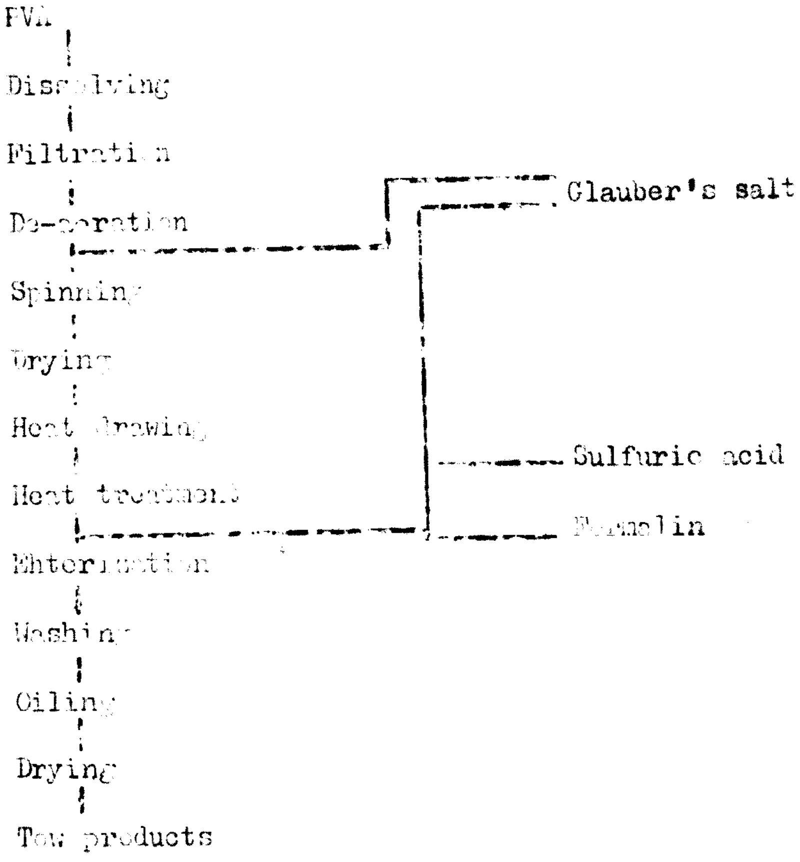
7. Manufacturing Process of Vinylon

Vinylon is manufactured by dry-spinning and wet-spinning processes. The wet spinning process is employed for production of staple and tow. Both are used in making filaments.

7.1. Wet-Spinning Process

The most representative wet-spinning process is as follows and Figure 1 shows flow sheet for manufacturing vinylon tow.

Figure 1 Flow Sheet for Manufacturing Vinylon Tow



(1) Preparation of spinning solution: PVA removed of impurities such as sodium acetate is dissolved in a dissolving tank by a given amount of water to a given concentration (15 - 16%).

When PVA having relatively many residual acetic acid groups is used, PVA is resaponified before or after dissolution. The PVA solution is filtered with a filter press, then left standing for several hours in the de-aeration tank. In some cases titanium dioxide is added as matter [illegible] pigments or coloring matter. After dissolution, PVA aqueous solution must be maintained at temperatures higher than [illegible] to prevent gelatinization.

(2) Spinning: Spinning solution is extruded through the fine holes of spinnerets by a gear pump into the coagulating bath (saturated solution of Glauber's salt) maintained at around [illegible] - 40°C to be dehydrated and coagulated, thus PVA fibers being formed. Spinning machines are made in horizontal and vertical types. The fibres coming out from the coagulating bath are stretched by guides or rollers.

(3) Drawing and Heat Treatment: The PVA fibers after the spinning step are stretched in an aqueous salt solution maintained at a high temperature. After drying they are stretched in air at temperatures of 200 - 2[illegible]°C to improve the fiber properties. Then they are treated for several minutes at a temperature of [illegible] - 2[illegible]0°C under tension or tensionless condition. This significantly improves their hot water resistance.

(4) Etherization and Finishing: The PVA fibers after heat treatment have improved heat resistance, but are not yet insoluble. For the perfect hot water resistance, they are etherized with formaldehyde or other aldehydes. Then they are thoroughly washed, oiled and packed for shipment. In the case of staple fiber, fibers are crimped in the drawing and heat treatment stages or in the finishing stage after cutting.

7.2. Dry-Spinning Process

In the dry spinning process, solution preparation conditions and spinning process differ from those of the wet-spinning process. In the dry spinning of PVA, reducing the amount of water to be evaporated during spinning to the minimum is desirable since water has high latent heat development and a high boiling point. Therefore a solution in a concentration as high as [illegible]0 to 40% is used. This spinning solution is allowed to pass through the gear pump and candle filter in the spinning cylinder tube and is extruded through the fine holes of the spinnerets [illegible] into air [illegible] filaments. In dry spinning, washing for salt removal is not required, and therefore the filaments coming out through the spinnerets are directly stretched under dry heat. Stretching times are determined according to the properties demanded for the fiber by the market.

9. Processing of Vinylon

9.1. Spinning of Vinylon

Vinylon staple alone or in combination with natural fibers can be made into yarn having various characteristics depending on purpose and application.

(1) Short Fiber Spinning System

In the cotton spinning system or short fiber spinning systems of different types, fineness and length of vinylon staple as well as the kind and the proportion of other fibers to be blended are selected [illegible] the quality required for final products.

(2) Long Fiber Spinning System

[illegible] for industrial materials requiring especially high strength, a method of spinning long fibers made from tow [illegible]. In this method, slivers of long fiber length (average fiber length 100 - 1[illegible]0 mm) are made from tow with cutters or converters, then they are spun into yarn. Long fiber spinning systems include the Perlock system, the converter system and the turbo [illegible] system.

(3) Worsted and Woollen Spinning System

[illegible] blending with wool, etc. where spun yarn with the feel of worsted yarn is required, spinning is done by worsted or woollen system.

8.2. Weaving and Knitting

Since vinylon fibers have properties more resembling those of natural fibers than the other synthetic fibers, and are easily blended with other fibers, their woven and knitted products find extensive use for clothing and industrial purposes. For these purposes, conventional preparation followed by weaving and knitting machines can be used.

8.3. Dyeing

A vinylon fiber consists of skin and core. Dyestuffs do not penetrate into the dense skin layer and therefore they penetrate into the spongelike core through the grooves of the skin layer where they are absorbed. Chemically, OH groups and ether-bonds are side chains against the main chains $-(-CH_2-CH)_n$. With a low degree of etherization and many OH groups, dyeing is possible by the use of dyestuffs such as direct dyes, sulphur dyes, vat dyes and naphthol dyes which exhibit affinity to OH groups. However, as the degree of etherization becomes higher, most of non-crystalline parts of the fibers where dyestuffs can be attached have become etherbonds. Then dyeing is more readily done by disperse dyes having affinity to ether-bonds. This means that changing the method or degree of etherization can control the dyeability of the products. Vinylon prepared by the dry-spinning process has a uniform cross section structure and therefore highly bright coloured products can be obtained by using partially amino-etherized PVA. Dyeing activity of vinylon depends largely on dyeing temperature; [illegible] dye absorption occurs at 80 - 90 °C.

9. Future Development

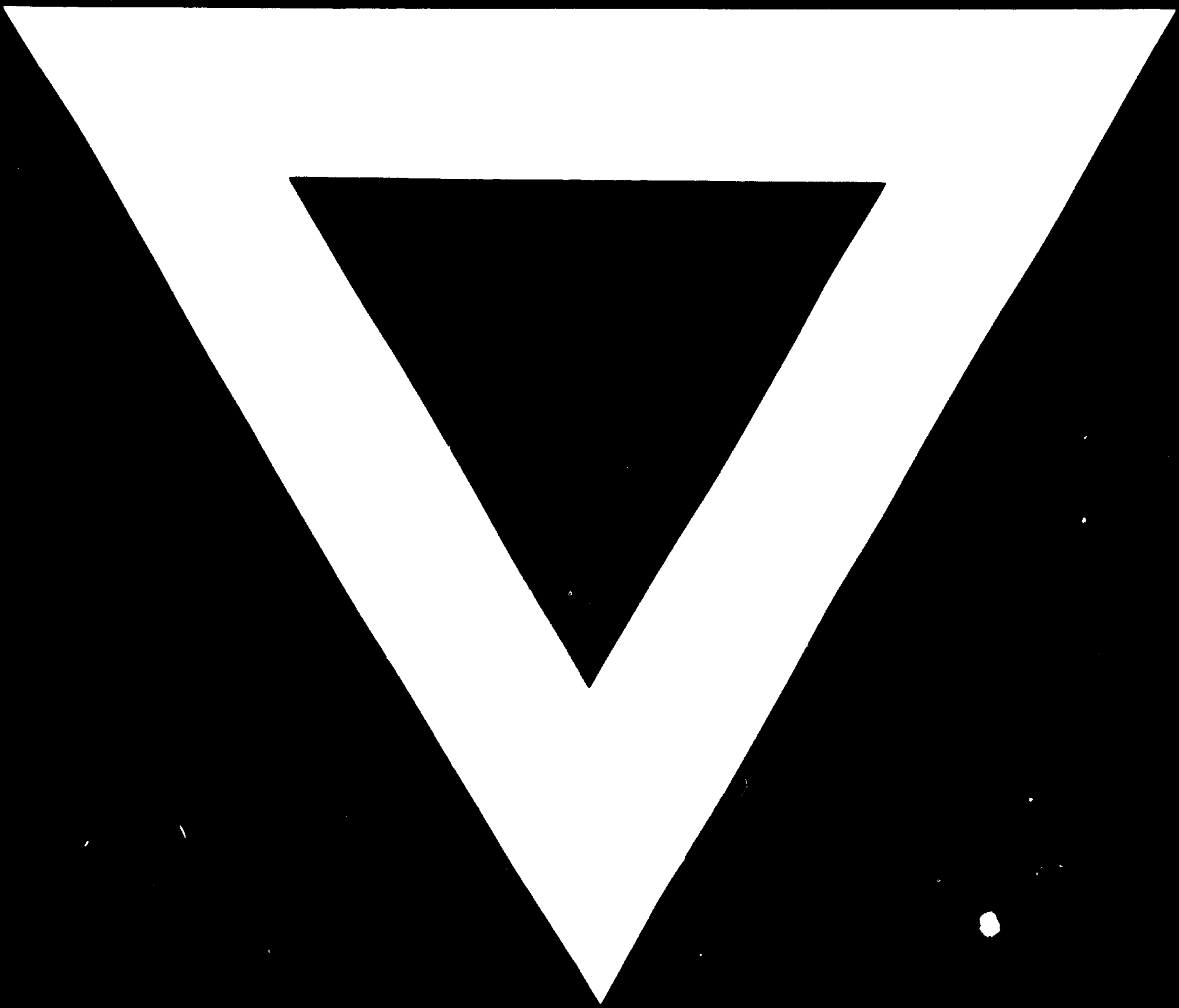
The vinylon industry in the future will develop steadily, based on the records having been accumulated so far. Also substantial qualitative changes can be foreseen.

In the first place carbide as raw material for PVA is shifting to natural gas, then to ethylene. In the early days of industrialization, there were just a few associated industries and we were dependent on the

PVA made from carbide in order to use easily accessible natural resources. However, as petrochemical industry progresses, dependency on the PVA from ethylene has become more advantageous in the economical aspects. This implies the fact that the vinylon industry has come to have closer connections with not only the textile industry but also the petrochemical industry and other chemical industries.

In the second place, the application of PVA in areas other than as raw materials for vinylon has [illegible]. During the rapidly growing period of the vinylon industry, the use of PVA in non-fiber applications was extremely limited. [illegible] independent industry. However, the trend [illegible] has gradually [illegible] the PVA market in this [illegible] PVA industry [illegible] established as an independent industry. The future PVA industry will find an increasingly large market in [illegible] and will achieve a vigorous growth.

In the third place, vinylon itself [illegible]. In the markets for fishing nets, [illegible] which has [illegible] the progress of vinylon, [illegible] replaced by the entry of other synthetic fibres [illegible] techniques developed, [illegible] new [illegible] industrial purposes [illegible] fabrics, [illegible] fabrics, [illegible], materials requiring [illegible], [illegible] vinylon's advantages are [illegible] international markets, vinylon will play an increasingly important role [illegible] its outstanding property combinations.



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