

Study of Cellulose Raw Materials for Celluloid

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Cellulose, the main raw material of celluloid, was in principle used after refining linters. However, there were also periods in which other raw materials were used. This was investigated chronologically, and the factors behind it were examined.

Since the situation differed from company to company, corporate histories were first investigated in order to grasp the situation at each of the major companies. By reviewing these together, the changes in the procurement of cellulose sources for celluloid in Japan were clarified. In addition, the factors that led to this course of development were considered.

1. Status of Cellulose Raw Material Procurement at Each Company

Descriptions concerning cellulose sources were extracted by company from accessible company histories and prior survey literature. The companies surveyed were chosen on the basis of "ease of obtaining information," and therefore are not representative of the celluloid industry as a whole. Furthermore, several years are required from the planning of a business, through construction and actual operation of a plant, until products are shipped. For this reason, it is difficult to determine at what point actual procurement began. Even among prior surveys, there are discrepancies of two or three years. The following list is intended to reflect the actual situation as closely as possible, but given this characteristic of the dates, please understand that it indicates only approximate periods.

(1) Dainippon Celluloid, Sakai Plant, Aboshi Plant (Daicel) ⁽¹⁾

Meiji 43 (1910): Purchase of tissue paper (Oji Paper, Toyo Paper)

Taisho 8 (1919): In-house production of tissue paper at Sakai,

Showa 8 (1933): Transfer of the papermaking process to Aboshi (for production of photographic printing paper for Fuji Film)

Showa 11 (1936): Owing to the sharp rise in rag prices, linters were produced in-house in Tianjin. Thereafter, linter plants were established in Mokpo, Manchuria, and elsewhere.

To process the in-house linters, a linter refining process was installed at Aboshi.

Showa 12 (1937): The Pure Cotton Prohibition Order was issued, making domestically produced rags unusable.

Showa 24 (1949): Paper mill put into operation

(2) Takigawa Celluloid (Takiron) ⁽²⁾

Taisho 2 (1913): Purchase of tissue paper

Showa 22 (1947): Start of in-house paper production

The process diagram shows that the facility was equipped with a spherical digester, bleaching, papermaking, and drying, indicating that raw linters were used as the raw material.

(3) Taisei Kako ⁽³⁾

Taisho 9 (1920): Since the founding of its nitrocellulose business, the company purchased and used tissue paper (from Taihei Paper, Awa Paper, and others).

(4) Tsutsunaka Celluloid ⁽⁴⁾

Showa 4 (1929): Production of nitrocellulose began, but the raw material, tissue paper, was purchased.

(5) Tajima Kako (Taihei Chemical Products) ^(5, 6)

Taisho 5 (1916): Production of collodion by pot-type nitration

Showa 13 (1938): Start of nitrocellulose production

Showa 24 (1949): Start of celluloid production (linter pulp, wood pulp)

(6) Nitchitsu Explosives (Asahi Kasei)⁽⁷⁾

Showa 9 (1934): Start of manufacture of nitrocellulose for explosives, using linters⁽⁸⁾

Showa 11 (1936): Start of Chissoloid production (tissue paper purchased from Oji Paper)

Showa 13 (1938): In-house production of tissue paper

2. Changes in Cellulose Sources

Around Meiji 20 (1887), as the applications of celluloid expanded, there were cases in which businesses that had been processing imported celluloid sheet attempted to produce the sheet themselves. At that time there was insufficient knowledge, and the process amounted to little more than placing rags or wastepaper (in Japan, used clothing and wastepaper had been reused since the Edo period) into a jar (the only acid-resistant vessel readily at hand was a ceramic jar), adding nitric acid and sulfuric acid, and stirring. Linters were not known as a cellulose source, and they were difficult to obtain. Since the quantities produced were small, the volumes required could also be covered through rag collection channels.

A major change occurred around Meiji 40 (1907). Both the Mitsui and Mitsubishi zaibatsu built celluloid plants and invited foreign engineers. In addition, in order to promote the use of camphor, the Government-General of Taiwan translated and published the foreign technical work "Celluloid Manufacturing Methods" in Meiji 41 (1908). At the plants built during this period, the cellulose source was used in the form of tissue paper, which was purchased from paper manufacturers. For paper manufacturers, tissue paper for celluloid was a "specialty paper" produced on a small scale. For this reason, the digesters were also very small units known as spherical digesters, which allowed flexible operation: raw material blends were adjusted to meet the performance required for each demand, and cooking and refining conditions were varied. Initially the main materials were the rags traditionally used and the cotton waste generated by spinning companies, but it can be inferred that as volumes expanded, linters also began to be used. A switch to wood pulp was of course constantly kept in mind, but the required quality could not be secured and it could not be used for celluloid.

Once celluloid production was on track, in-house production of tissue paper began. Dainippon Celluloid began papermaking at Sakai in Taisho 8 (1919).

In Showa 9 (1934), Nitchitsu Explosives began using linters, drawing on the knowledge gained from Bemberg, which it had commercialized separately.

Later, around the time the Great Depression had been weathered, a worldwide shortage of cellulose sources arose. This was because demand for nitrocellulose for explosives grew as a result of conflicts in various regions and of military expansion. To cope with this, in Showa 11 (1936) Dainippon Celluloid established a linter plant in Tianjin, China, building a system of self-sufficiency in linters. To refine the raw linters obtained there, a refining process was installed at Aboshi, completing an integrated production system for cellulose sources.

The changes in cellulose sources in Japan's celluloid industry are summarized in Table 1 (next page).

Table 1: Changes in Methods of Procuring Cellulose Sources for Celluloid

	Production form	Cellulose source	
~M40 (1907)	Handicraft industry	Rags, spinning waste, etc.	
M41 (1908)~	Modern industrial production	Purchase of tissue paper	(Procured by paper manufacturers)
T8 (1919)~		In-house production of tissue paper	Refined linters
S9 (1934)~		Integrated production	Raw linters

Each company chose a procurement method suited to its own business development. Takigawa completed its integrated system in Showa 22 (1947). Tajima, Taisei, and Tsutsunaka continued to purchase the material in the form of tissue paper. Nitchitsu Explosives had been engaged in the nitrocellulose business and others before entering celluloid (Chissoloid), and it possessed papermaking and linter refining functions within its group; accordingly, apart from a period during start-up when it procured tissue paper from Oji Paper, it carried out integrated production from raw linters.

3. Various Factors in the Selection of Cellulose Sources ^(9, 10)

(1) Orientation toward wood pulp

Because linters were expensive compared with wood pulp and their supply was unstable, there was a constant intention to convert to wood pulp. This tendency was particularly strong among the paper manufacturers that supplied tissue paper, as they possessed a wide range of information on cellulose sources.

In fact, viscose rayon and cellulose acetate (acetate) switched almost completely to wood pulp. Even in nitrocellulose, there are fields such as coatings and explosives in which wood pulp is used.

Wood pulp for viscose is called dissolving pulp (abbreviated as DP); it has a high alpha-cellulose content and a high degree of polymerization. It is produced by pulping softwood with a high cellulose content by the sulfite process (SP) and increasing the alpha-cellulose ratio in a refining step.

Celluloid made using wood pulp is said to be inferior in physical properties such as strength and to yellow readily. It also exhibited turbidity and could not be used for transparent applications. There was also the problem that the nitration reaction did not proceed readily, and these issues could not be resolved. Strength is considered to be attributable to the degree of polymerization, yellowing to residual lignin, and turbidity to residual hemicellulose and beta-cellulose.

In celluloid, the era in which the raw material took the form of tissue paper continued for a long time. This is said to be because the uniformity of the nitration reaction would otherwise be impaired, but the reason is not well understood. The influence of secondary structure, such as crystallinity and crystal size, may also be involved. In the first place, the nitration reaction is a solid (cellulose)–liquid (nitric acid) reaction and therefore tends to be nonuniform. Even in the case of linters, the tissue paper was invariably finely shredded before being charged, which suggests that subtle requirements existed for making the solid/liquid reaction proceed more uniformly.

(2) Orientation toward avoiding rags

It can be presumed that in the handicraft era, used clothing and old cotton wadding were the principal raw materials. In Japan, the recycling of used clothing and the refluffing of old cotton wadding had been widely practiced since the Edo period. Moreover, since most of the common people's clothing was cotton or hemp and thus almost entirely cellulosic, the risk of contamination with foreign

materials was small. However, because decolorization could not be carried out well, only white cotton was sorted out from the rags visually and by hand.

As industrialization advanced and the spinning and rayon businesses arose, the problem of blended fabrics emerged. Advances in blending technology made the sorting of rags difficult. In particular, once the wartime regime took hold, the "Pure Cotton Prohibition Order" was issued and blending with rayon (low alpha content and low degree of polymerization) became mandatory, rags could no longer be used as a raw material for celluloid.

(3) Influence of preceding and concurrently operated businesses

Dainippon Celluloid took the opportunity of producing base paper for photographic printing paper as part of its photographic film business to bring the papermaking process for celluloid tissue paper in-house.

Tajima Kako's founding business was collodion (a nitrocellulose solution), and since a lower solution viscosity was preferable, it had little attachment to linters.

Nitchitsu Explosives started out from guncotton. It had in-house divisions manufacturing cuprammonium rayon (Bemberg) and tissue paper (for dynamite packaging and for rayon refining), and thus possessed abundant knowledge of cellulose sources and processing methods. For this reason, from the outset it was able to use raw linters as its raw material and to produce tissue paper in-house.

In addition, fields other than celluloid as a molding material—such as coating raw materials, film, and cellulose acetate—have property requirements that differ from those for celluloid raw materials. It is possible that cellulose sources were reviewed on the occasion of operating these businesses concurrently. We intend to pursue further investigation from this perspective.

(4) Social factors

a. War

The greatest influence is exerted by war. In World War I, the celluloid plants of the belligerent nations were mobilized for guncotton production, bringing about shortages of celluloid and of cellulose sources. Japan, being far from the battlefields, took on the role of making up for these shortages.

During the period when Japan pursued military expansion, from the Sino-Japanese War through to the Pacific War, Japanese celluloid plants were converted to guncotton production, so celluloid production was constrained.

Cotton cultivation and the cotton spinning industry are found throughout the world, but there are still many regions that use only lint and do not utilize linters. Whenever cellulose sources ran short, demand was met by expanding the areas from which linters were collected. One example is Dainippon Celluloid's entry into raw linter production in China and elsewhere during the Sino-Japanese War.

b. Industrial structure ⁽¹¹⁾

Linters, the principal cellulose source for celluloid, were a waste product of the cotton spinning industry, and edible oil is co-produced during linter production. Cotton-growing areas, spinning mills and oil-extraction plants, and the areas where textile products and edible oils are consumed are not necessarily located in the same region; the existence of all of these, together with their linkage through a distribution system, is a prerequisite for linter production.

In the United States, the birthplace of the celluloid industry, all of these elements existed domestically, and it can therefore be seen that linters came to be positioned as a cellulose source. In other regions, it was necessary to deliberately establish such operations or to link them together. In postwar Japan as well, the production of cottonseed oil began, and domestically produced linters came to be manufactured. ⁽¹¹⁾

The role of the paper manufacturing industry was also significant. Many celluloid factories purchased it from paper companies in the form of tissue paper. Paper companies were, so to speak, the professionals of cellulose. In Japan in particular, with its tradition of washi (Japanese paper), there was strong demand for cellulose with long fiber lengths, for such uses as banknotes, securities, partition papers, and calligraphy paper. To meet this demand, they possessed technologies for utilizing old clothing and linter pulp (in the United States, purified linters were distributed on the market), and were thus able to respond to the requirements of the celluloid industry.

c. Recycling system

As stated earlier, when processing craftsmen were attempting to produce celluloid base material, lint derived from old clothing was available as a cellulose source. In Japan, the recycling of textiles had been carried out quite routinely in daily life since the Edo period. This became their source of cellulose. However, once modern factories were launched and volumes expanded, procurement through this route became difficult, and, with knowledge gained from abroad, a gradual shift to linters took place.

4. Summary and Outlook

The main raw materials of celluloid are cellulose, camphor, and nitric acid. Of these, camphor was deeply connected with the administration of Taiwan, and has therefore attracted considerable interest and been examined in various forms. Nitric acid underwent a transition from the saltpeter process to the ammonia oxidation process; since it is an inorganic chemical with few quality-related problems, the conversion was made on the basis of cost, at the same time as in the fertilizer industry and other sectors.

By contrast, the cellulose source presented quality issues even after the era in which wood pulp became mainstream, and linters continued to be used. Moreover, raw material procurement depended in part on paper companies, and research in this field has lagged behind.

In this paper, the transition of cellulose sources was investigated by examining the research results of our predecessors, company histories, and other materials. Much remains unclear, and this may have only increased the number of research topics. We wish to continue our examination further.

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