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Heritage Science

REVIEW

Statistics of the early synthetic dye industry

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Abstract

From the invention of Perkin's Mauve in 1856, to publication of the first edition of the *Colour Index* in 1924, more than 1200 synthetic organic colourants were introduced. Some achieved commercial success, while others were rarely used for reasons such as high cost, low fastness, and toxicity. This turbulent period of innovation was largely driven by demand of the textile industry; however, synthetic colourants were subsequently adopted in many other applications. An understanding of the most common materials and their properties is therefore important to the study of heritage collections and their preservation. The risk of light damage during exhibition of objects is often a concern due to the fugitive nature of many synthetic colourants.

To provide a foundation for focused research on synthetic dye identification and lightfastness, work was carried out to identify the most prominent of these colourants used in North America up to the year 1924 when the first edition of the *Colour Index* was published. Information was compiled and analysed from several sources including multiple editions of the *Colour Index*, and government documents related to the manufacture and trade of synthetic dyes that provide data from 1914 onwards. Cross-referencing between the information sources provided a summary of parameters for each colourant including the date of introduction, number of manufacturers, lightfastness, and quantity produced or imported in the United States.

A document published in 1916 by the US Department of Commerce listed 259 colours with Schultz number imported during the 1913–1914 fiscal year, in quantities above 10,000 lb (4536 kg). Adding domestic products to the list, and removing duplicates, gave 289 individual colours with Schultz number imported and/or produced in the US. In addition, there were some imports of unknown composition: 96 azo, 23 sulphur, and 68 unclassified. Further review of census data from 1917 through the 1920's suggested that less than one quarter of the dyes listed in the *Colour Index* were imported or manufactured in significant amounts. The results of this analysis are presented as summary statistics, which are complemented by an open dataset publication to facilitate future research.

Keywords: Synthetic dyes, Identification, Lightfastness

Introduction

Early advances related to synthetic and semi-synthetic dyes were made by Barth (indigo carmine, 1743) [1], Woulfe (picric acid, 1771) [2], Scheele (murexide, 1776) [3], and Runge (aurin, 1834) [2, 4]; however, a commercial industry was not significant until William Perkin created mauveine in 1856. This was followed by a period of accelerated developments of new products, which peaked near the end of the 19th century. Early synthetic dyes are generally categorised according to chemical structure. The most abundant synthetic dyes belong to the azo class. However, other chemical classes, including triphenylmethane, azine, xanthene, nitro, oxazine, indigoid and anthraquinone have each in turn had an important impact on the industry. As colourants were introduced to the market, many were used to colour materials other than textiles: e.g. waxes and varnishes, writing and printing inks, paint pigments, and early plastics. As a result, large quantities of synthetic colourants are present throughout museum collections around the world. Detailed reviews of the early industry [2, 3, 5–9] and respective dye chemistry [10–14] are plentiful in the

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literature, and provide valuable context for current studies of heritage materials.

For many heritage objects, efforts are made to identify colourant materials for historical study, authentication and dating, and fastness evaluation. The large number of possible compounds makes it an overwhelming task to characterise them all, and in many cases reference materials are scarce. Analysis of these colourants is further complicated by the varied nomenclature used by manufacturers, where similar names were used for different dyes. The confusing letter codes (markings) after dye names, practice of mixing products, and mischaracterization of the product composition create additional layers of complexity. Norton [15] offers insight into some aspects of this confusing issue in a section titled "The Marks of Coal-Tar Colors". As just one example of the complexity, Norton indicated that 300,000 lb of a dye named Cotton Black with various markings (unclassified by Schultz #) was imported into the United States in 1914. The first edition of the *Colour Index* (CI) contains several listings that relate to this product name [16]: Cotton Black from Wülfing, Dahl & Co. (CI# 994); Cotton Black B, 3B, BG BGN BGNX, BN, C from BASF (azo direct dyes with no CI#); Cotton Black E extra from BASF (CI# 581); Cotton Black G, 2G, 3G, PF extra, R, RN from BASF (azo direct dyes with no CI#); and Cotton Black RW extra from BASF (CI# 582). In some cases, a classified dye may also have a spectrum of possible compositions depending on the production method. An example is given by Crace-Calvert [17] when discussing the methyl and ethyl-rosanilines, and the production of various forms of Hofmann's Violet:

> *...by varying the circumstances of experiment, instead of three of the hydrogen being replaced by ethyl, dyes may be obtained having two, or only one, replaced by ethyl; moreover, by substituting methyl iodide for ethyl iodide, corresponding methyl compounds may be prepared. In this way Hofmann violets are obtained of different shades, varying from RRR, the very red, which is principally a salt of monomethylated rosaniline* $C_{28}H_{18}(CH_3)N_3$*, to BBB, the bluest shade.*

In the 1980s, Schweppe [18, 19] aimed to simplify the problem by providing a shortlist of 65 early synthetic organic dyes with notes to assist with their identification, while also highlighting a subset of 22 stated as the most common [20]. In the field of heritage science, this list has become a common reference despite the ambiguous selection criteria. In a review of the early synthetic dyes, Barnett [20] remarks that areas for further work include identifying the most common materials using 19th century trade literature, and compiling respective fastness data. The challenge, of course, is finding quantitative data regarding dye production or use. The *Colour Index* is an encyclopaedic resource of colourant data; however, information related to the degree of use is limited, and modern lightfastness data is unavailable for many of the earliest materials. Similarly, most trade books of the period simply outline the vast range of products available. It is likely that a significant number of the catalogued products were rarely used, and analysis could be prioritized to specific materials given the appropriate information.

This study investigates several trends in the synthetic dye industry using early 20th century literature: multiple editions of the CI [16, 21, 22], Norton's census [15], and the annual *Census of Dyes and Coal Tar Chemicals* from the US Tariff Commission [23, 24]. The goal of the work is to provide a framework to better understand the most prominent early synthetic dyes, optimise methods for identification, and further develop lightfastness data for risk assessment tools. Findings are presented as summary statistics due to the large number of materials, while tabulated values are provided in a complementary dataset for further research work [25].

Data mining the colour index

Many reference texts were published with lists of dyes during the latter half of the 19th century, leading to the development of different classification systems [26]. The first widely adopted approach was *Tabellarische übersicht der Künstlichen Organischen Farbstoffe* by Schultz and Julius [27], which was published in seven editions between 1888 and 1931. The fifth edition [28], retitled *Farbstofftabellen*, became a template for the first edition of the CI and resulted in a legal dispute between the two groups [26]. The CI employed a new numbering system, and provided a convenient table for cross-referencing with listings in *Farbstofftabellen.* The table is a valuable resource since it allows conversion from the 1914 Schultz number to the first CI number [16], and subsequently to the CI constitution number in current use [21]. This conversion was applied in the following section during a review of census data, where US dye imports and production quantities were published with the 1914 Schultz number prior to 1924.

The CI contains a large amount of information showing interesting trends when extracted and studied as a dataset. For example, a column of citations for each dye provides the approximate date of introduction for each compound. Using this information, the earliest date was tabulated for each dye, and a sorted list was used to generate a plot of cumulative dyes invented through time. The result in Fig. 1 shows a sigmoid curve with features characteristic of the stages of an evolving technology:

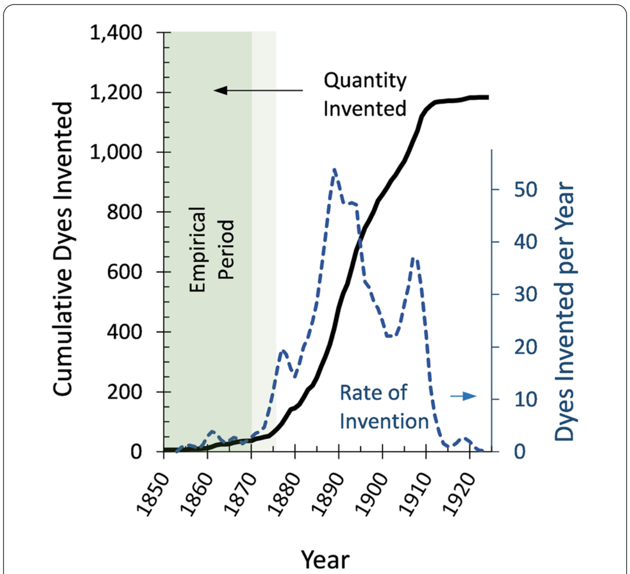

Fig. 1 Cumulative number of synthetic dyes invented by year, compared with the rate of dye invention. The dashed line represents the annual quantity of dyes invented, calculated as a moving rate of invention over five-year intervals (secondary y-axis)

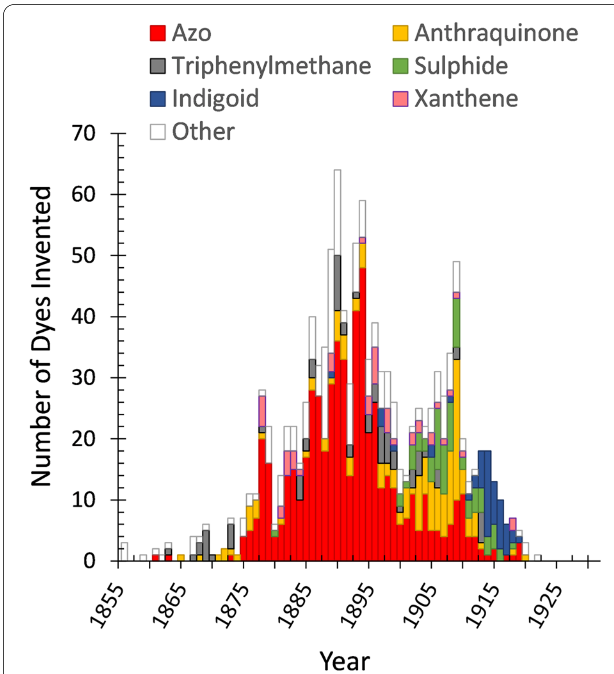

Fig. 2 Number of synthetic dyes invented by year and chemical class

birth, development, maturity and stagnation. At a conference celebrating the centennial of Perkin's creation of mauveine, Lecher [5] described the stage up to ~1870 as the 'empirical period' when the structural theory was not yet established. This was followed by the 'rational period', as the Kekulé structure of benzene was developed in 1865 [29] and later accepted. When the industry entered this latter period, the introduction of new dyes accelerated as specific organic compounds were sought after. This is evident in Fig. 1, where the rate of dye introduction accelerates shortly after 1870, and peaks around 1889. Another moment of significance is observed at the year 1893, when 50% of this first wave of dyes was introduced.

Further information is added to this overview of the early synthetic dye industry by cross-referencing date of introduction with chemical classification. The stacked histogram in Fig. 2 highlights the distribution of dyes invented over time by chemical class, with a dominant peak generated by the azos around 1890 (cf. Fig. 1). A smaller peak at 1907 is due to the development of anthraquinone and sulphur dyes, which is followed by a cluster of indigoids around 1915. The introduction of triphenylmethane and xanthene dyes is scattered throughout the time period, along with the remainder of chemical classes grouped as 'other' to simplify the plot.

The CI provides occasional qualitative indications of popularity in the descriptive text for the listed dyes, but the information is sparse and of limited use. Another potential popularity indicator is the number of manufacturers, M, that offered each product. One would assume that compounds having many manufacturers would also experience significant commercial use. Those with one manufacturer may have had patent protection; however, this was likely circumvented or ignored using different methods of manufacture and varied rules by country. Gardener [30] provides a compilation of articles related to the British coal-tar industry, with the issue of patent protection highlighted throughout the text. In one paper, Bloxam [31] states "The whole of organic chemistry has been wondrously advanced by the desire of the maker of dyestuffs on the one hand to obtain monopolies of new colours, and on the other hand to avoid paying royalties under existing patents". To illustrate the varied number of manufacturers, Fig. 3 shows a plot of the number of dyes having more than a given value of M – defined here as the manufacturers in exceedance, M_e. The plot was constructed in this manner to quickly determine how many colourants would be required for future analysis (e.g. chemical and lightfastness) if we target those with more than some threshold number of manufacturers. Nearly all dyes had one or more manufacturers, while less than 50% had $M \geq 3$, and only ~10% are indicated with $M \geq 15$. The number of manufacturers is also used in the following section when plotting import and production quantities from US census data.

A final parameter investigated in the CI was the lightfastness rating for each colourant. The third edition [22] was reviewed for ISO and AATCC lightfastness values

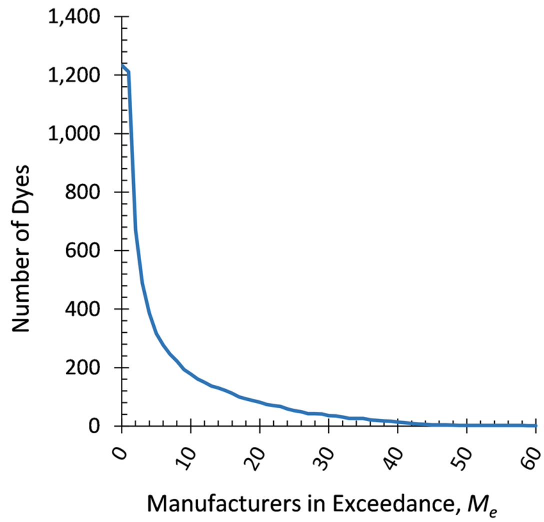

Fig. 3 Number of dyes listed in the *Colour Index*, 1st ed. versus number of manufacturers in exceedance

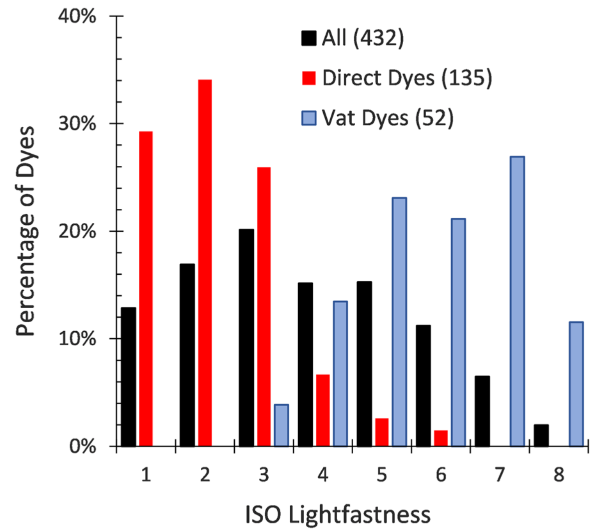

Fig. 4 ISO lightfastness ratings in the third edition of the Colour Index [22], for colourants listed in the first edition [16]. Data selected for normal depth of shade, and direct dyeing without aftertreatment where applicable. ISO values for mordant dyes primarily relate to wool with chrome mordant. A small number of duplicates with the same CI generic name was removed for this plot

related to each of the 1,230 synthetic organic dyes listed in the first edition [16], using a conversion table in the second edition [21] for the two CI numbering systems. In total, 432 were found, or ~35% of the total list. Counts of dyes with half-step ratings (e.g. ISO 2–3) were split equally into adjacent bins of full step ISO values to plot a histogram of the quantity of dyes with each lightfastness. Figure 4 shows the resulting percentage of dyes having each ISO value, with a peak at ISO 3. This distribution is affected by the number of dyes with ISO ratings listed in the CI, which varies significantly by chemical class and application type. The distributions are also highlighted separately for the direct and vat dyes, showing peaks at the lower and higher ISO ratings respectively. Figure 5 gives a related plot in which the relationship between the ISO and AATCC lightfastness scales is evaluated using data from 237 of the dyes, where both measures were available.

Many of the earliest synthetic dyes were highly fugitive to light, which is well documented in literature of the period [32]. When Lauth discussed a new dye (Violet de Paris) in 1867, he gave some perspective on the shifting public opinion toward lightfastness:

> *The violets obtained from methyl-aniline possess a richness and purity which leave nothing to be desired … Nevertheless they were not adopted by manufacturers, who, indeed at the time above mentioned (1861), attached less importance to the beauty of a colour than to its permanence. In this latter respect the methyl-aniline violets do not excel, and consequently dyers would have nothing to do with them. Gradually, however, people have become accustomed to colours which fade on exposure to the solar rays. Indeed the public taste at the present day, in colours as in everything else, inclines rather to tinsel than to solid excellence.*

In his 1896 Hofmann memorial lecture, Perkin [6] also points to the shift of public interest toward new

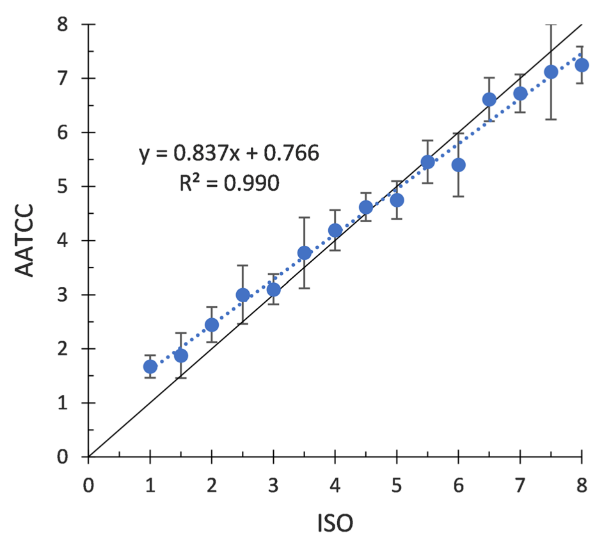

Fig. 5 Relationship between AATCC and ISO lightfastness ratings for 237 dyes listed in the Colour Index, 1st and 3rd editions. 90% confidence intervals shown from the student t-test.

vibrant colours at the expense of fastness. In a later review of the industry, Whittaker [33] comments on the unfortunate discovery of so many fugitive dyes during the early development of the industry:

> *"The basic dyes supply the next series of milestones. I have always felt that it was a tragedy that these dyes, of still unsurpassed brilliant hues coupled with extreme fugitiveness, were discovered so early in the development of synthetic dyes. Their lack of fastness retarded the use of the then so-called "Anilines" for years, and provided the old-time dyers with a strong justification for their hostility and conservatism. The other misfortune was that these brilliant hues found their way into the textile designers' studios, and were repeatedly sent to the dyers for reproduction in a fastness for which there were no comparable dyes. For example, Malachite Green was discovered in 1878, but the dyer had to wait until 1920 for Caledon Jade Green, which first enabled him to give with confidence a Jade Green hue suitable for soft furnishings and washing fabrics. Meantime dyers were compelled to write thousands of letters regretting inability to dye the hues requested. The leading basic dyes appeared in the following sequence-Magenta (1858), Methyl Violet (1866), Methylene Blue (1876), Malachite Green (1878), Auramine 0 (1883), whilst Rhodamine B followed in 1887 and Rhodamine 6G in 1892."*

When reviewing the extensive list of materials in the first edition of the CI, it is natural to wonder which materials were used in significant quantities, and most likely prevalent in museum collections. The CI was developed as a catalogue of all colourants, but only provides occasional information about popularity using qualitative terms such as 'used extensively for…'. It is possible that many of the colourants were never used in significant quantities, while others achieved varying degrees of popularity. Some colourants are known to have had a period of success prior to their replacement by a new dye with improved properties and/or simplified production methods. An example is found in the history of the earliest synthetic green dyes. Cherpin created the first of value called aldehyde green in 1862, which was later displaced by Perkins green, iodine green, and methyl green. The CI notes the prior popularity for many of these dyes, as well as their replacement and ultimate obsolescence. Although limited quantitative data exists regarding the use of earliest synthetic dyes, valuable information is available from United States census data starting in 1913–1914. The following section provides an overview of data collected from government documents of the period.

US imports and domestic production

A resource for assessing general dye popularity is the US census data published in the early 20th century, at a time when there was significant pressure to boost domestic production and compete with manufacturers in Europe. The outbreak of World War I in July 1914 led to a severe disruption of the dye industry due to the broad reliance on supplies from Germany. This included finished products, as well as the large number of intermediates for dye manufacture. The issue was often described as the 'dyestuff famine' or 'dyestuff crisis' [34, 35], and short-lived attempts were made to return to traditional methods using natural dyes [36] with limited success. Commenting on the state of the US dye industry, Hesse [34] made the following observations in November 1914:

> *At or about the end of 1912, 76 different chemical dyes were made in this country; today 100 such are made – in two years a 33 per cent increase; the United States market probably has no fewer than 900 different chemical dyes, each of them in active use, some of them to a very small extent, others to a very large extent and, no doubt, many of each of these could be eliminated and their places taken by others now on the market.*

At approximately the same time, the mystery regarding US dye imports was addressed by a commercial agent named Thomas H. Norton at the US Department of Commerce (Fig. 6). With careful planning to avoid the pitfalls experienced by similar efforts in Britain, Norton successfully conducted a census of imports for the 1913–1914 fiscal year [15]. His report included a large table of import quantities above 10,000 lb. (4536 kg), dollar values, commercial dye name, and Schultz number where available. These quantities were evaluated in the present study by converting the Schultz numbers to those of the first CI edition. Figure 7a shows the quantities reported by Norton versus CI number, with markers at the top indicating many of the chemical classes. The top-ten imported dyes are noted with labels on the peaks, and outlined in Table 1. Further information is provided in Appendix: Table 2, and the accompanying dataset [25]. Norton also catalogued dyes without a Schultz number; however, these only amounted to ~16% of the total import quantity (see

Fig. 6 Thomas H. Norton (1851–1941). Source: Oesper Collections in the History of Chemistry, University of Cincinnati [37]. Used with permission

Appendix: Table 3 for those above 100,000 lb). The results of Fig. 7a provide a useful indication of which dyes were predominantly used in the US when domestic manufacturing was still maturing.

A related development from Norton's census was the US Revenue Act of 1916. This led to the formation of the Tariff Commission, and enacted measures to temporarily support the US dyestuff industry through trade policy. As a means of tracking progress, an annual report was published by the Tariff Commission starting in 1918 (with 1917 data) called the *Census of Dyes and Coal-Tar Chemicals*. The report continued for several decades, with each issue summarising quantitative data regarding dye production and imports by chemical classification number (i.e. Schultz prior to 1924, followed by early CI#). For the current study, a review of these data was undertaken by tabulating production amounts from 1917 through the 1920's. Conversion to first edition CI number also allowed cross-referencing with data summarised in the previous section. Figure 7b and c show imports and domestic production data respectively for 1920, where the log-scale highlights the large quantities of some dyes. Unlike Norton's census, subsequent publications list amounts below 10,000 lb (not shown here); however, some domestic production data was withheld to maintain manufacturer privacy. A small group, particularly sulphur dyes, included production amounts but were not characterised by Schultz number.

Figure 8a presents US imports for the 1914 fiscal year versus the number of manufacturers listed in the first edition of the CI for the respective dyes. A similar plot is given in Fig. 8b, showing peak annual production for the period of 1917–1924 versus number of manufacturers. There is significant scatter in these data; however, the plots indicate a trend of increasing dye quantities with number of manufacturers. In both plots, data points circled in red indicate one of the 65 dyes in the Schweppe list [18]. Bracketed numbers in the legends give the number of points plotted for each series. For example, Fig. 8a shows 259 materials imported into the US in quantities greater than 10,000 lb, of which 43 are described by Schweppe. Dyes imported in large quantities, and not in Schweppe's list, may be worth further examination if the CI describes applications relevant to heritage objects.

Disruption to the dye industry during WWI contributed to the United States domestically producing many of the dyes that were previously imported in significant quantities. Figure 9 explores this trend with a plot of the production and imports of dyes in the United States during 1920 versus 1914 imports (Norton's census) for the corresponding materials. By 1920, approximately one third were produced in the US in quantities significantly larger than the prior 1914 imports. Some continued to be imported (41 %); however, these were typically at much lower quantities. A small number (6 %) were both imported and produced in the US during 1920, with production dominant.

A broader assessment of census data from 1917 through the 1920's suggests that less than one quarter of the colourants in the CI were produced or imported in the United States in significant quantities during the period. In comparison, Norton's census listed 259 colours with Schultz number imported in quantities above 10,000 lb (~ 21 % of the CI) during the 1913–1914 fiscal year. Adding the list of domestic products (tabulated by Norton without quantities), and removing duplicates, gave 289 compounds with unique Schultz number that were imported and/or produced in the US. There were also several imports of unknown composition in Norton's census: 96 azo, 23 sulphur, and 68 unclassified. This likely included duplicate counts of similar compounds. See Appendix: Table 3 for the small subset of undefined dyes imported in amounts over 100,000 lb. The overall findings emphasize that a subset of the CI list is worth greater attention for further analysis. It is also important to note that some applications of concern to heritage collections may have used colourants in relatively small amounts that are overshadowed by these general statistics.

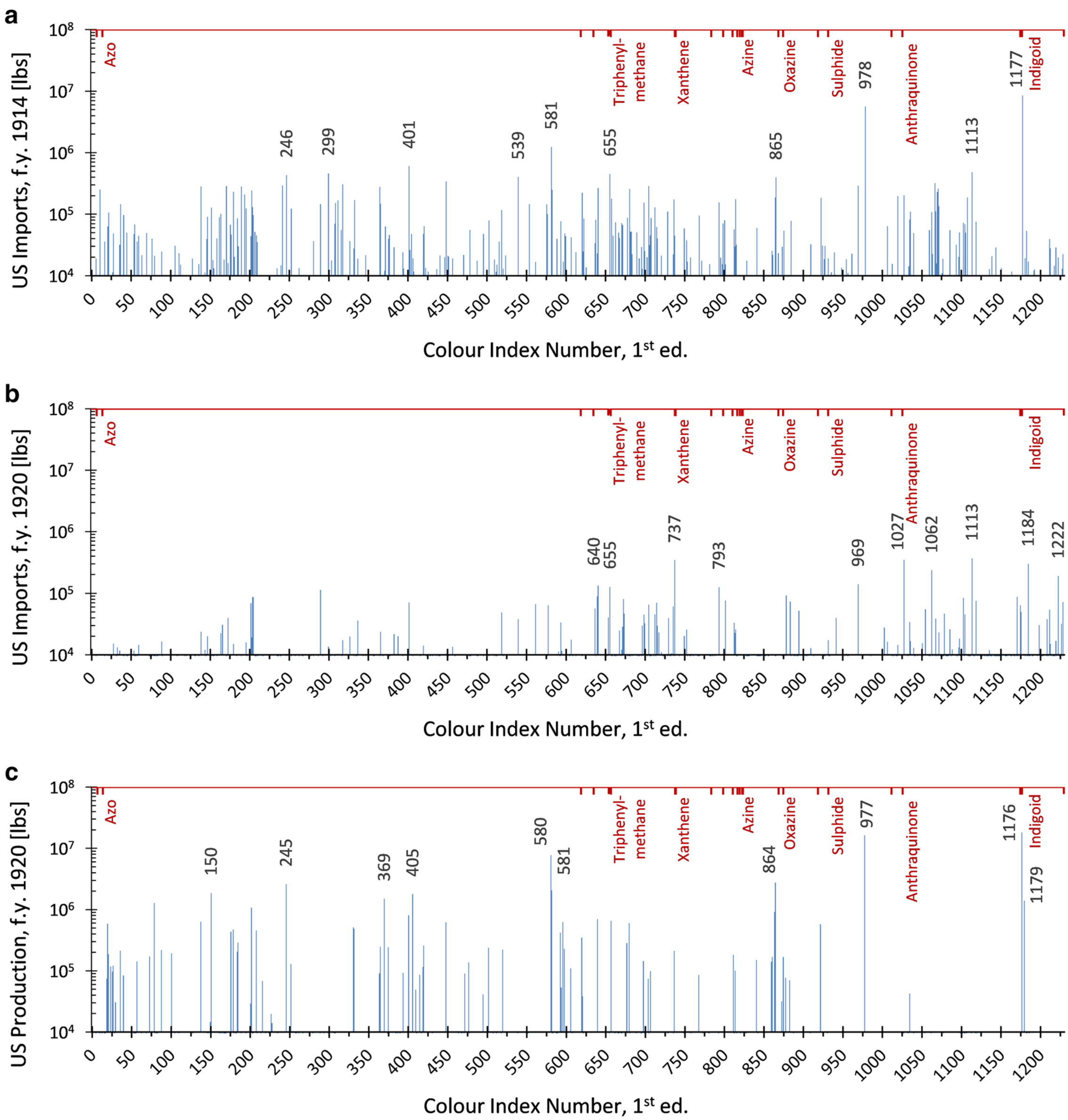

Fig. 7 Quantity of dyes imported or produced in the United States versus 1st ed. Colour Index number: **a** 1914 imports from Norton's census; **b** 1920 imports; **c** 1920 production. Labels shown for the 10 largest values. See Appendix for descriptions of the labelled dyes

Conclusions

Statistics of the early synthetic dye industry were reviewed by extracting colourant data from the CI including date of introduction, number of manufacturers, chemical class, and lightfastness. These parameters were plotted to show trends with respect to the number of dyes introduced over time, the rate of introduction, and the types of colourants from the mid-19th century to 1924. The number of manufacturers was shown as a potential indicator of popularity with values ranging from zero to more than 60 per colourant. Lightfastness data with ISO and AATCC ratings were summarised by cross-referencing between multiple editions of the CI. This was used to highlight the relationship between ISO and AATCC rating systems, and also the distribution of ISO lightfastness for 432 colourants listed in the 1st edition of the CI.

The analysis of CI data was followed by a review of United States census literature from 1914 through the 1920's. In broad terms, census data suggested that less

Table 1 Top ten dyes imported into the United States in 1914

Rank	Schultz # 1914	CI # 1st ed.	CI # 2nd ed.	Generic Name	Class	~Date Intro.	*M*	Imports lb x 10^3
1	874	1177	73,000	Vat Blue 1	Indigoid	1890	13	8507
2	720	978	53,185	Sulphur Black 1	Sulphur	1896	23	5615
3	462	581	30,235	Direct Black 38	Trisazo	1901	39	1238
4	333	401	22,590	Direct Blue 2	Disazo	1890	32	606
5	842	1113	69,825	Vat Blue 6	Anthraquinone Vat	1903	6	479
6	275	299	26,695 see also 26,750; 26,751	Mordant Black 5	Disazo	1889	24	460
7	493	655	41,000; 41000B	Basic Yellow 2; Solvent Yellow 34	Ketonimine	1883	18	449
8	217	246	20,470	Acid Black 1	Disazo	1891	42	429
9	436	539	31,560	Direct Black 9	Trisazo	1896	14	403
10	700	865	50,420	Acid Black 2	Azine	1867	41	395

Schultz # (1914) is shown from source data, along with the conversions to first and second edition CI numbers. Approximate date of introduction and number of manufacturers are given from the 1st ed. of the CI

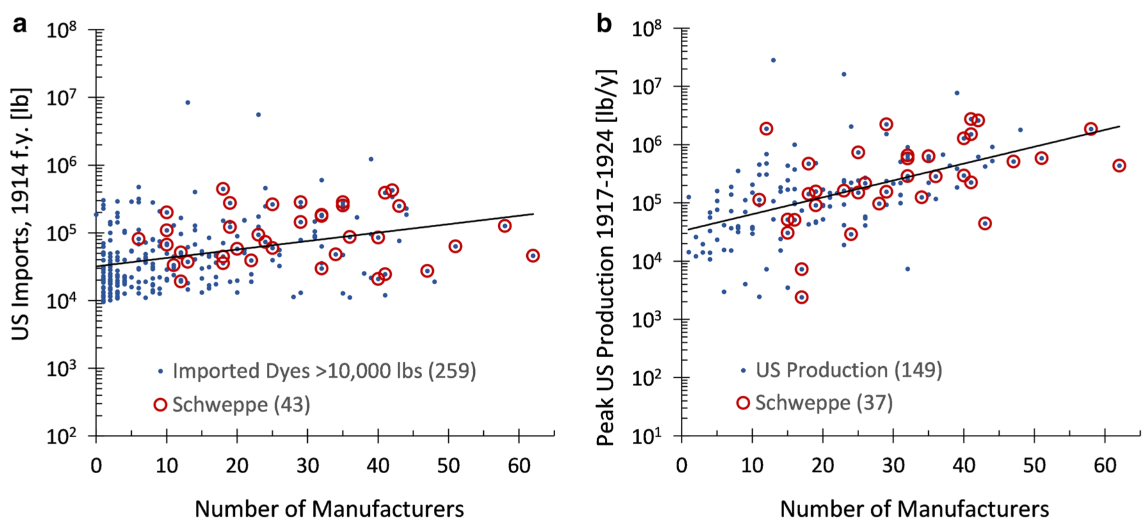

Fig. 8 Imports and production of dyes in the United States versus the number of manufacturers listed in the Colour Index for each colourant: **a** imports during the 1914 fiscal year; **b** peak annual production reported during the period of 1917–1924

than a quarter of the colourants listed in the 1st edition of the CI were imported or produced in the US in significant amounts. Norton's earlier census for 1913–1914 listed 259 colours with Schultz number imported to the US in quantities above 10,000 lb (~21% of the CI), and a total of 289 classified (Schultz #) compounds imported and/or produced. There were also several compounds of unknown composition in Norton's census that made up ~16% of total imports: 96 azo, 23 sulphur, and 68 unclassified. Census data were further used to show the amounts of each colourant imported and produced in the US, which was then compared with the number of manufacturers. Comparisons were also made with the Schweppe list of synthetic dyes since it is frequently used as a reference for dye analysis. Several of the dyes on Schweppe's list were imported or produced in significant quantities during the studied time period; however, the results highlight that many other products deserve further consideration.

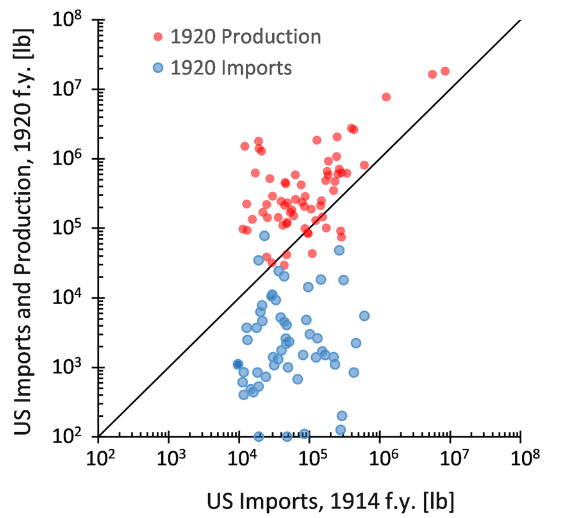

Fig. 9 Comparison of US imports of dyes in 1914 with domestic production and imports for the same dyes in 1920

To support research related to the history and preservation of heritage collections, a compilation of the tabulated values is provided as an open dataset [25]. In our ongoing work, this information provides a tool for selecting specific samples of interest for chemical analysis and lightfastness testing using a set of criteria: introduced 1870 and earlier (empirical period); produced or imported in large quantities (≥ 100,000 lb/yr); having a large number of manufacturers listed in the CI ($M \geq 15$); or historically significant. Appendix: Table 2 provides a summary of colourants meeting these criteria, while the dataset [25] allows anyone to generate a custom list based on parameters of interest.

In parallel to the work described here, a list of available period samples was tabulated from trade books and dying texts (i.e. commercial name, and manufacturer where available). This was cross-referenced with the first edition of the *Colour Index* to verify the CI# where possible, and then pick the target samples of interest for analysis. At the present time, over 100 samples have been studied for the effects of light exposure with a custom fadometer, and chemical markers using gas chromatography-mass spectrometry (GC-MS). The goal is to provide an open database for researchers to explore the results, and build upon in future work. Finally, the samples with and without light damage are catalogued and stored for possible analysis with other analytical techniques.

Appendix

Table 2 gives a summary of dyes in the first edition of the CI [16] that meet one or more of the following criteria: (a) introduced 1870 or earlier; (b) imported or produced in quantities of 100,000 lb/yr or more (1914–1924); (c) having 15 or more manufacturers listed in the CI. Matches for each criterion are emphasised in bold and underlined for clarity. A question mark in the column of peak annual US production (1917–1924) indicates that the dye was produced in at least one reporting period; however, the quantity was withheld for manufacturer privacy. This list of dyes is also supplemented with some materials of known relevance or historical significance that are not already captured: e.g. the first sulphur dye (CI 933), and early dyes without CI number (aldehyde green, aldehyde blue). Additionally, cross-referencing with the Schweppe list [18] of important early synthetic dyes showed a near match for Mordant Red 3 (CI 1034): introduced ~ 1871, with nearly 82,000 lb imported to the US in 1914. The dye was added to the table in consideration of these factors.

Table 2 List of dyes fulfilling selection criteria based on date of introduction (≤ 1870), number of manufacturers (≥ 15), US imports and production (≥ 100,000 lb/yr), or other significance

CI # (1st ed.) [16]	CI Constitution # [21]	CI Generic Name [21]	Chemical Class [16]	Approx. Date of Introduction [16]	Manufacturers [16]	US Imports, lb x10^3 (1914) [15]	US Imports, lb x10^3 (1920) [23]	Peak US Production, lb/yr x10^3 (1917-1924) [23, 24]	Schweppe Listed [18]
2	10005	Mordant Green 4	Nitroso	1875	**17**	-	-	-	N
5	10020	Acid Green 1	Nitroso	1885	**19**	19.1	0.500	45.9	N
7	10305		Nitro	**1849**	12	-	-	-	Y
8	10310		Nitro	**1869**	1	-	-	-	N
9	10315	Acid Yellow 24	Nitro	**1856**	**24**	-	-	-	Y
10	10316	Acid Yellow 1; Food Yellow 1	Nitro	1879	**43**	**250**	-	44.5	Y
15	11000	Solvent Yellow 1	Monoazo	**1861**	**20**	-	-	52.3	N
16	13015	Acid Yellow 9	Monoazo	1877	**32**	36.0	8.38	7.3	N
17	11160; 37210	Solvent Yellow 3; Azoic Diazo Component 4	Monoazo	1877	**19**	-	-	48.1	N
19	11020	Solvent Yellow 2	Monoazo	1876	**16**	-	-	**101**	N
20	11270; 11270B	Basic Orange 2; Solvent Orange 3	Monoazo	1875	**51**	63.3	-	**586**	Y
21	11320; 11320B	Basic Orange 1; Solvent Orange 4	Monoazo	1877	**31**	**106**	3.31	**221**	N
23	11920	Solvent Orange 1	Monoazo	1875	**20**	-	-	?	N
24	12055	Solvent Yellow 14	Monoazo	1883	**36**	-	-	**117**	N
26	15970	Acid Orange 12	Monoazo	1878	**28**	11.4	-	96.6	Y
27	16230	Acid Orange 10; Food Orange 4	Monoazo	1878	**34**	48.5	15.3	**124**	Y
28	16100	Acid Orange 14	Monoazo	1878	**19**	-	-	?	Y
30	17200	Acid Red 33; Food Red 12	Monoazo	1890	**15**	-	-	30.7	Y
31	18050	Acid Red 1	Monoazo	1902	**26**	-	7.03	**218**	Y
36	14025	Mordant Yellow 1	Monoazo	1887	**29**	**145**	-	**2233**	Y
40	14030		Monoazo	1885	**39**	96.5	1.20	**386**	N
53	16580	Acid Violet 3	Monoazo	1891	**16**	47.1	11.8	**173**	N
56	16600	Acid Violet 6	Monoazo	1890	5	-	-	**108**	N
57	18055	Acid Violet 7	Monoazo	1902	**18**	36.0	0.100	**143**	Y
63	16010; 16011	Acid Orange 16	Monoazo	1879	**15**	21.5	-	?	N
69	12120	Pigment Red 3	Monoazo	1905	**17**	49.7	-	?	N
73	12140	Solvent Orange 7	Monoazo	1883	**24**	-	2.21	**171**	N
78	16020	Acid Orange 17	Monoazo	1879	**23**	-	0.500	18.9	N
79	16150	Acid Red 26	Monoazo	1878	**40**	21.0	1.92	**1285**	Y
81	12020	Solvent Brown 5	Monoazo	1878	**18**	-	-	?	N
82	12170	Solvent Red 4; Pigment Red 40	Monoazo	?	**20**	-	0.500	?	N
88	16180	Acid Red 17	Monoazo	1878	**41**	24.7	16.5	**224**	Y
89	16250	Acid Red 44	Monoazo	1883	**16**	-	0.331	-	Y
101	see 11290, 11300, 11335		Monoazo	1898	12	-	-	**474**	N
135	12210	Basic Blue 16	Monoazo	1886	**16**	15.4	0.055	?	N
138	13065	Acid Yellow 36	Monoazo	1879	**35**	**285**	23.8	**629**	Y
142	13025	Acid Orange 52	Monoazo	1875	**15**	-	-	?	N
143	13080	Acid Orange 5	Monoazo	1876	**36**	11.2	12.0	?	Y
145	13090	Acid Orange 1	Monoazo	1880	**22**	39.3	10.4	-	Y
146	13096		Monoazo	1880	**31**	90.5	20.1	**138**	N

Table 2 (continued)

148	14270	Acid Orange 6	Monoazo	1875	**28**	-	-	?	Y
150	14600	Acid Orange 20	Monoazo	1876	**24**	-	1.32	29.0	Y
151	15510	Acid Orange 7	Monoazo	1876	**58**	**128**	2.30	**1850**	Y
161	15575	Acid Orange 8	Monoazo	1887	**20**	90.2	-	88.8	N
163	15850	Pigment Red 57	Monoazo	1903	4	**101**	22.6	68.4	N
165	15585	Pigment Red 53	Monoazo	1902	5	-	30.8	**161**	N
170	16500	Mordant Black 9	Monoazo	1902	6	**285**	2.80	?	N
176	15620	Acid Red 88	Monoazo	1877	**62**	46.4	-	**434**	Y
179	14720	Acid Red 14; Food Red 3	Monoazo	1883	**44**	**231**	15.1	**527**	N
180	14835	Acid Red 12	Monoazo	?	10	20.1	-	**206**	N
182	16045	Acid Red 13	Monoazo	1878	**26**	-	-	?	Y
184	16185	Acid Red 27; Food Red 9	Monoazo	1878	**40**	85.5	9.86	**294**	Y
185	16255	Acid Red 18	Monoazo	1878	**32**	30.0	-	**289**	Y
189	15630	Pigment Red 49	Monoazo	1899	8	**282**	0.220	**353**	N
193	15640	Acid Red 10	Monoazo	1882	9	**209**	-	?	N
195	14095	Mordant Yellow 3	Monoazo	1890	**23**	**124**	15.9	94.2	N
202	15705	Mordant Black 17	Monoazo	1903	**29**	**243**	19.2	**1523**	N
203	14645	Mordant Black 11	Monoazo	1904	11	**130**	87.2	**303**	N
204	15710	Mordant Black 1	Monoazo	1904	12	96.6	87.3	**687**	N
208	13390	Acid Blue 92	Monoazo	1897	11	45.0	8.62	**454**	N
216	16105	Mordant Red 9; Pigment Red 60	Monoazo	?	13	-	1.75	**107**	N
234	20170	Acid Orange 24	Disazo	1881	**20**	13.2	5.24	**169**	N
241	20350	Acid Black 17	Disazo	1891	5	**291**	-	?	N
246	20470	Acid Black 1	Disazo	1891	**42**	**429**	6.67	**2609**	Y
248	26100	Solvent Red 23	Disazo	1879	**24**	-	-	?	N
252	27290	Acid Red 73	Disazo	1882	**19**	**123**	3.06	**158**	Y
258	26105	Solvent Red 24	Disazo	?	**23**	-	-	41.4	N
262	27200; see also 27201	Acid Red 115	Disazo	1879	**15**	13.2	0.550	51.8	Y
280	26905	Acid Red 66	Disazo	1879	**17**	36.6	2.34	74.2	N
289	26400	Acid Blue 120	Disazo	1892	**19**	**146**	**114**	**481**	N
299	26695; see also 26750 and 26751	Mordant Black 5	Disazo	1889	**24**	**460**	13.7	**223**	N
307	26370	Acid Black 24	Disazo	1902	10	69.6	2.40	**150**	N
308	26300	Acid Black 7	Disazo	1888	**18**	**152**	-	43.0	N
311	27240		Disazo	1885	12	**168**	-	?	N
317	27725	Direct Blue 132	Disazo	1893	1	**306**	17.3	?	N
326	see 29150-29230		Disazo	1900	7	36.7	19.9	**188**	N
331	21000	Basic Brown 1	Disazo	**1863**	**47**	27.6	0.114	**514**	Y
332	21010	Basic Brown 4	Disazo	1878	**37**	**171**	-	**673**	N
364	24890	Direct Yellow 4	Disazo	1886	**19**	**277**	0.250	91.2	Y
365	24895	Direct Yellow 12	Disazo	1886	**31**	**148**	23.8	**508**	N
370	22120	Direct Red 28	Disazo	1884	**41**	12.0	10.1	**1503**	Y
375	22145	Direct Red 10	Disazo	1886	**25**	39.7	-	**243**	N
376	22150	Direct Red 17	Disazo	1891	**17**	46.1	6.20	?	N
394	22570	Direct Violet 1	Disazo	1889	**29**	13.1	-	92.5	N
401	22590	Direct Blue 2	Disazo	1890	**32**	**606**	71.2	**905**	N
406	22610	Direct Blue 6	Disazo	1890	**48**	19.0	1.10	**1790**	N
410	22250	Direct Yellow 1	Disazo	1884	**26**	-	-	54.3	N
415	22130	Direct Orange 8	Disazo	1887	**16**	-	1.20	96.5	N

Table 2 (continued)

419	22310	Direct Red 1	Disazo	1889	**35**	47.7	14.1	**139**	N
420	22311	Direct Brown 2	Disazo	1889	**32**	63.7	-	**258**	N
446	23370	Direct Orange 10	Disazo	1886	**20**	19.9	-	?	N
448	23500	Direct Red 2	Disazo	1884	**42**	**342**	10.5	**618**	N
461	23520	Direct Violet 21	Disazo	1885	**16**	-	-	-	N
472	23710	Direct Blue 21	Disazo	1890	**20**	-	-	92.2	N
477	23850	Direct Blue 14	Disazo	1890	**30**	-	1.10	**216**	N
478	23380	Direct Orange 7	Disazo	1888	**21**	55.6	3.81	?	N
495	24100	Direct Red 7	Disazo	1885	**26**	47.7	4.30	41.3	N
502	24140	Direct Blue 8	Disazo	1885	**29**	78.7	3.07	**237**	N
512	24280	Direct Blue 22	Disazo	1894	9	15.2	1.46	**112**	N
518	24410	Direct Blue 1	Disazo	1891	**23**	**117**	48.9	**245**	N
520	24400	Direct Blue 15	Disazo	1890	**35**	12.9	7.51	**223**	N
539	31560	Direct Black 9	Trisazo	1896	14	**403**	38.0	**185**	N
553	31820		Trisazo	1896	2	**146**	-	-	N
575	31940		Trisazo	1893	3	**144**	-	-	N
576	31955	Direct Blue 30	Trisazo	1890	2	**100**	0.300	?	N
581	30235	Direct Black 38	Trisazo	1901	**39**	**1238**	-	**7737**	N
582	30245	Direct Black 4	Trisazo	1901	**24**	**249**	-	**2051**	N
593	30295	Direct Green 6	Trisazo	1891	**43**	76.6	33.3	**420**	N
594	30315	Direct Green 8	Trisazo	1891	**31**	-	11.6	**137**	N
596	30045	Direct Brown 1	Trisazo	?	**16**	17.0	-	**1000**	N
598	30140	Direct Brown 6	Trisazo	1888	**15**	48.7	-	**245**	N
606	35005	Direct Brown 44	Polyazo	1887	7	41.9	17.7	**138**	N
620	40000	Direct Yellow 11	Stilbene	1883	**35**	**222**	0.841	**570**	N
621	40015; 40002	Direct Orange 15	Stilbene	1888	**22**	24.7	-	**147**	N
622	40006	Direct Yellow 6	Stilbene	1886	**16**	85.1	-	?	N
636	18820	Acid Yellow 11	Pyrazolone	1892	11	33.5	56.6	**113**	Y
640	19140	Acid Yellow 23; Food Yellow 4	Pyrazolone	1884	**25**	**266**	**133**	**736**	Y
655	41000; 41000B	Basic Yellow 2; Solvent Yellow 34	Ketonimine	1883	**18**	**449**	**127**	**471**	Y
657	42000; 42000B	Basic Green 4; Solvent Green 1	Triphenylmethane	1878	**32**	**179**	2.04	**654**	Y
662	42040	Basic Green 1	Triphenylmethane	1879	**24**	73.9	3.30	?	Y
670	42095	Acid Green 5; Food Green 2	Triphenylmethane	1879	**18**	71.4	12.2	?	N
677	42510; 42510B	Basic Violet 14; Solvent Red 41	Triphenylmethane	**1856**	**36**	87.1	2.09	**284**	Y
679	42530		Triphenylmethane	**1863**	12	-	1.05	-	N
680	42535; 42535B	Basic Violet 1; Solvent Violet 8	Triphenylmethane	**1861**	**35**	**255**	3.23	**632**	Y
683	42536	Basic Violet 13	Triphenylmethane	**1866**	**17**	22.4	0.095	?	N
684	42585	Basic Blue 20	Triphenylmethane	1871	5	-	-	-	N
685	42590		Triphenylmethane	**1866**	4	-	-	-	N
686	42556		Triphenylmethane	**1866**	0	-	-	-	N
687	42515		Triphenylmethane	**1860**	2	-	-	-	N
688	42760	Solvent Blue 23	Triphenylmethane	**1866**	5	-	-	-	N
689	42775	Solvent Blue 3	Triphenylmethane	**1861**	**21**	50.6	-	87.5	N
692	42685	Acid Violet 19	Triphenylmethane	1877	**22**	19.1	4.85	-	N
698	42650	Acid Violet 17	Triphenylmethane	1890	**21**	**154**	45.2	**148**	N
703	42765	Acid Blue 119	Triphenylmethane	**1862**	**15**	-	-	?	N
704	42750	Acid Blue 110	Triphenylmethane	**1862**	**29**	**287**	65.4	**155**	Y
705	42770	Acid Blue 48	Triphenylmethane	**1862**	**16**	31.5	1.82	?	N
706	42780	Acid Blue 93	Triphenylmethane	**1862**	**18**	45.0	2.15	?	Y

Table 2 (continued)

707	42755	Acid Blue 22	Triphenylmethane	**1862**	**31**	86.5	6.72	98.8	N
712	42051	Acid Blue 3	Triphenylmethane	1888	14	**129**	45.5	?	N
724	43800		Triphenylmethane	**1834**	3	-	1.46	?	N
725	43875		Triphenylmethane	**1835**	0	-	-	-	N
728	44040	Basic Blue 11	Triphenylmethane	1892	10	**110**	0.097	?	Y
736	44095	Acid Blue 97	Triphenylmethane	1895	3	**174**	4.18	?	N
737	44090	Acid Green 50	Triphenylmethane	1883	**16**	44.9	**342**	**376**	N
749	45170	Basic Violet 10	Xanthene	1887	**20**	58.3	20.3	?	Y
766	45350	Acid Yellow 73	Xanthene	1871	**17**	-	0.725	2.4	Y
768	45380	Acid Red 87	Xanthene	1871	**23**	94.5	0.209	**161**	Y
771	45400	Acid Red 91	Xanthene	1875	**17**	17.5	-	-	N
773	45430	Acid Red 51; Food Red 14	Xanthene	1876	**17**	-	-	7.3	Y
793	46045	Basic Orange 15	Acridine	**1862**	**21**	**155**	**126**	**123**	N
801	47005	Acid Yellow 3	Quinoline	1882	**16**	15.3	76.5	51.2	Y
806			Quinoline	**1856**	2	-	-	-	N
812	49000	Direct Yellow 59	Thiazole	1887	**26**	56.2	33.1	**271**	N
813	19540	Direct Yellow 9	Thiazole	1887	**15**	29.9	22.6	3.5	N
814	19555	Direct Yellow 28	Thiazole	1887	**23**	**175**	25.9	**230**	N
821	49700		Indophenol	1881	1	-	-	**127**	N
841	50240	Basic Red 2	Azine	**1859**	**25**	59.9	2.61	**150**	Y
846	50245		Azine	**1856**	2	-	0.057	-	Y
857	50375	Basic Red 6	Azine	**1868**	1	-	-	-	N
860	50400	Solvent Blue 7	Azine	**1863**	**38**	25.3	-	**436**	N
861	50405	Acid Blue 20	Azine	**1867**	**39**	21.8	-	**184**	N
864	50415; 50415B	Solvent Black 5; Solvent Black 7	Azine	**1867**	**44**	**187**	0.220	**919**	N
865	50420	Acid Black 2	Azine	**1867**	**41**	**395**	0.250	**2743**	Y
870*	50440	Oxidation Base 1; Pigment Black 1	Aniline Black	**1834**	1	-	-	-	N
875	see 76060	Oxidation Base 10	Aniline Black	1888	**15**	53.7	0.300	**168**	N
883	51030	Mordant Blue 10	Oxazine	1881	**15**	-	73.3	**435**	N
909	51175	Basic Blue 6	Oxazine	1879	**26**	32.5	12.9	58.3	N
922	52015	Basic Blue 9	Thiazine	1876	**32**	**186**	10.2	**577**	Y
933	53210; 53000		Sulphide	1873	8	-	1.5	-	N
969†	53630	Vat Blue 43	Sulphide	1908	3	**293**	**141**	-	N
978	53185	Sulphur Black 1	Sulphide	1896	**23**	**5615**	-	**16305**	N
1016	55005		Hydroxyketone	**1828**	1	-	-	-	N
1019	57010	Mordant Black 37	Hydroxyketone	**1861**	3	**198**	14.5	-	N
1027	58000	Mordant Red 11; Pigment Red 83 (lake)	Anthraquinone	**1868**	10	**202**	**348**	?	Y
1034	58005	Mordant Red 3	Anthraquinone	1871	6	81.9	34.2	?	Y
1035	58200	Mordant Brown 42	Anthraquinone	1877	14	**110**	16.7	**157**	N
1043	58220		Anthraquinone	**1865**	0	-	-	-	N
1052	58600		Anthraquinone	**1835**	1	-	-	0	N
1054	63010	Acid Blue 45	Anthraquinone	1897	12	-	55.4	**309**	N
1062	58605	Mordant Blue 32	Anthraquinone	1891	4	**108**	**234**	56.5	N
1066	67410		Anthraquinone	1877	6	**319**	8.50	0	N
1067	67415	Mordant Blue 27	Anthraquinone	1881	6	**112**	38.8	0	N
1069	67425		Anthraquinone	1890	1	**230**	-	0	N
1070	67430		Anthraquinone	1890	1	**260**	2.00	0	N
1071			Anthraquinone	1888	2	**135**	23.2	0	N
1107			Anthraquinone Vat	1901	0	**187**	9.68	?	N
1113	69825	Vat Blue 6	Anthraquinone Vat	1903	6	**479**	**367**	?	N
1177	73000	Vat Blue 1	Indigoid	1890	13	**8507**	-	**28347**	N
1180	73015	Acid Blue 74; Food Blue 1	Indigoid	1890	12	19.3	4.53	**1877**	Y
1184	73065	Vat Blue 5	Indigoid	1907	8	16.9	**299**	?	N
1222	73620		Indigoid	1906	1	19.8	**190**	0	N
-	-	Aldehyde Green [14]	Triphenylmethane	1862	-	-	-	-	N
-	-	Aldehyde Blue [17]	Triphenylmethane	1861	-	-	-	-	N

Underlined bold values indicate matches to the selection criteria

*CI#870 may also be CI# 871 (from Schultz # 922 in source data); †CI# 969 may also be CI# 970 or 971 (from Schultz # 748 in source data)

Table 3 US dye imports in 1914 [15] exceeding 100,000 lb, without Schultz number

Product Name	Import Qty. lb x 10^3	Category
Benzo Fast Black L.	100	Unidentified azo
Oxy Diamine Black (V. M.)	147	Unidentified azo
Oxy Diaminogen (V. M.)	139	Unidentified azo
Cotton Black (V. M.)	300	Unidentified azo
Lake Red (V. M.)	349	Unidentified azo
Zambesi Black (V. M.)	629	Unidentified azo
Wool Black (V. M.)	119	Unidentified
Amine Black (V. M.)	146	Unidentified
Black (V. M.)	139	Unidentified

V.M. indicates 'various markings' (e.g. 2B, BB etc)

For further comparison, Table 3 provides a supplementary list of ambiguous dyes that were listed in Norton's 1914 census [15] with import quantities above 100,000 lb. Six dyes were categorised as unidentified azo materials, while the remaining three were of unknown chemical class.

Abbreviation

CI: Colour Index.

Authors' contributions

EH compiled the dataset used in this study, and drafted the manuscript. JP provided significant input through edits and revisions. Both authors worked on the interpretation of data, and the selection criteria for targeted analysis of colourants in future work. All authors read and approved the final manuscript.

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Availability of data and materials

The dataset generated and analysed during the current study is available in the Harvard Dataverse repository, https://doi.org/10.7910/DVN/BK2CBX [25].

Competing interests

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