Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Historical Article

Enzo Ferroni (1921-2007): the History of an Eclectic Chemist

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Citation: Dei L. (2023) Enzo Ferroni (1921-2007): the History of an Eclectic Chemist. *Substantia* 7(2): 83-100. doi: 10.36253/Substantia-2055

Received: Feb 17, 2023

Revised: May 2, 2023

Just Accepted Online: May 3, 2023

Published: September 21, 2023

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Abstract. Enzo Ferroni (Florence, 25 March 1921 – 9 April 2007) was an Italian chemist, full professor in physical chemistry at the University of Florence, where he served as Rector from 1976 to 1979, a renowned international scientist who initiated a new branch of chemistry, that applied to cultural heritage conservation. The history of his scientific and academic life offers a particular interest in a half-century cross-section of the history of chemistry in Italy and the entire world. In particular, Ferroni developed the colloids, surface, and interface chemistry in Italy immediately after the Second World War in a country where it was almost non-existent, sensing the extraordinary potential of this branch of chemistry in the fields of basic and applied research. This paper aims to reconstruct the history of this eclectic chemist starting from his pioneering studies in Italy on colloids, surfaces, and interfaces that, after the Second World War, came to be widely popular within the international scientific literature following three milestones represented by the studies of the Nobel laureates in chemistry, Richard A. Zsigmondy (1925), Theodor Svedberg (1926), and Irving Langmuir (1932). Enzo Ferroni's far-sighted and visionary ideas concerning the investigation of these systems and others with biological implications by the nascent resonance spectroscopies and surface diffraction techniques were recognised and underlined as the revolutionary approach by ever more sophisticated instrumentations that were to characterise chemistry research to this day. The consecration of the extraordinary potential and peculiarities of colloids, surfaces, and interfaces would come to fruition in 1991 with the Nobel laureate in physics Pierre-Gilles de Gennes, who finally discovered that "the methods developed to study ordinary phenomena in simple systems can be generalised to more complex states of matter, especially liquid crystals, and polymers" (official motivation of the Prize), recognising soft matter as a peculiar form of matter in the condensed phase. These pioneering frontiers in the newly established soft matter field can be considered Ferroni's last message in the bottle to young researchers facing the twenty-first century. The eclecticism of this chemist emerged from two other compelling aspects that are illustrated in this article: the chemistry for cultural heritage that Ferroni conceived, pushed by the dramatic damages suffered by the works of art after the Florence flood in 1966, and his strong vision about the equal dignity of basic and applied research, that led him to establish fruitful relationships with industries aimed to enhance technological fallouts, as the research by the Nobel laureates in chemistry (1963) Giulio Natta and Karl Ziegler had clearly shown.

Keywords: history of 20^{th}-century chemistry, colloids, surfaces and interfaces, chemistry for cultural heritage conservation, fundamental and applied research, soft matter.

1. INTRODUCTION

From the vantage point of the second fifth of the 21st century we have the possibility to look at the history of science of the second half of the 20th century with the eyes of the science historian, considering that all the discoveries made after the end of the Second World War until the beginning of the new century can be considered as sufficiently sedimented to re-evaluate them in a historical perspective.[1] The advance of science and technology in every field during such period was tremendous, and the people devoted to its progress have exponentially increased. Every discipline underwent an extraordinary multiplication of specialisations; simultaneously, science and technology had the need to be increasingly more multi- and inter-disciplinary. Moreover, science and technology started to create bridges towards human and social sciences in a sort of total globalisation of knowledge. In this frame, many scientists in every part of the world substantially increased their cooperation and research groups in different countries developed the various topics of each discipline, creating centres of excellence able to attract young scholars interested in the progress of science and technology. In this context, Italy was a noteworthy case since it emerged from twenty years of darkness characterised by the totalitarian fascist regime with all the consequences for the freedom of research and teaching.

Until the end of the Second World War the biggest advances in science were mainly prerogative of the United States of America, Germany, and United Kingdom: as an example, Italy had earned only two Nobel prizes in physics (Enrico Fermi, 1938; Guglielmo Marconi, 1919) and one in medicine or physiology (Camillo Golgi, 1906), whereas three great writers received the Nobel Prize in literature (Giosuè Carducci, 1906; Grazia Deledda, 1926; Luigi Pirandello, 1934).[2] Chemistry had lived through a less prosperous period with respect to the glorious 19th century, where the giants Amedeo Avogadro[3] (Turin, 1776-1856), Stanislao Cannizzaro[4] (Palermo, 1826 – Rome, 1910), and Raffaele Piria[5] (Scilla, 1814 – Turin 1865) had dominated the world scenario.[6] Indeed, some important chemists worked in Italy in the first half of the 20th century: among them we can include Giacomo Ciamician[7] (Trieste, 1857 – Bologna, 1922), Nicola Parravano[8] (Fontana Liri, 1883 – Fiuggi, 1938), Emanuele Paternò[9] (Palermo, 1847 – 1935), Raffaello Nasini[10] (Siena, 1854 – Rome, 1931), and Mario Betti (1875 – 1942),[11] but nobody succeeded in gaining the same great renown as the Italian school of physics: the first Nobel Prize in chemistry – still the only one – will arrive in 1963 with Giulio Natta (Porto Maurizio, 1903 – Bergamo, 1979).[2] Due to the proximity of the second half of the 20th century with our times, apart from the Nobel laureate Giulio Natta,[12] the literature is quite scarce about chemists who have lived and worked in this period: as examples, we recognize interesting papers on Giovanni Battista Bonino (Genoa, 1899 – 1985)[13], Massimo Simonetta (Pella, 1920 – Milan, 1986),[14] Adolfo Quilico (Milan, 1902 – 1982),[8] Giovanni Canneri (Montelupo Fiorentino, 1897 – Florence, 1964),[7,8] Lamberto Malatesta (Milan, 1912 – 2007),[15] Piero Pino (Trieste, 1921 – Milan, 1989),[16] Eolo Scrocco (Tivoli, 1916 – Rome, 2012).[17]

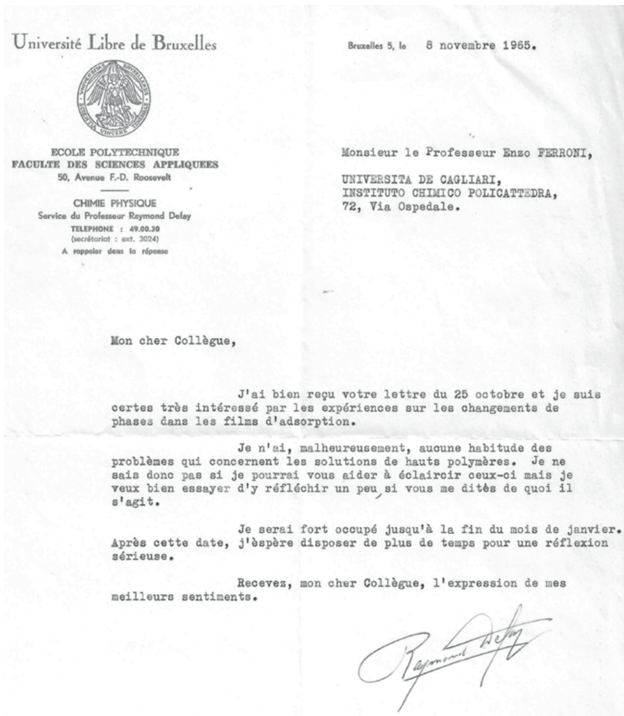
Since the present paper aims to report and discuss the work of the academic chemist Enzo Ferroni (Florence, 1921 – 2007), it seemed worthwhile to frame the scenario where he carried out most of his scientific activity, that is, the University of Florence. After the end of the Second World War, chemistry in Italy presented six main branches: analytical, industrial, inorganic, organic, pharmaceutical, and physical; inside each of these broad sub-disciplines, there were some specialisations within which, during the following decades, some important centres of excellence developed. At the University of Florence, inorganic chemistry took the path of coordination chemistry thanks to work initiated by Luigi Sacconi (Santa Croce sull'Arno, 1911 – Florence, 1992).[18] As far as organic chemistry is concerned, the path set by Angelo Angeli (Tarcento, 1864 – Florence, 1931)[8,19] and Adolfo Quilico (Milan, 1902 – 1982)[8,19] who moved to the Politecnico di Milan in 1943, was followed by Giovanni Speroni (Florence, 1910 – 1984).[8,19] Analytical chemistry was led by the already mentioned Giovanni Canneri. In contrast, pharmaceutical chemistry had two key scientists, Sergio Berlingozzi (Montevarchi, 1890 – Fiesole, 1957) and Mario Torquato Passerini (Casellina e Torri, now Scandicci, 1891 – Florence, 1962).[8,19] Industrial chemistry started to develop precisely in the period subject of the present study thanks to the work of Franco Piacenti (Florence, 1927 – 2002).[20] The chair of physical chemistry, the discipline that Enzo Ferroni selected for his chemistry master's degree thesis, was held by Giorgio Piccardi (Florence, 1895 – Riccione, 1972), a significant Italian scientist, though for some aspects quite controversial.[21] Enzo Ferroni defended his chemistry master's thesis (from now on, it will be used for this title the verb to graduate) in 1945 *magnum cum laude*, under the supervision of Giorgio Piccardi. The title of his work was "*Recent advances and opinions on chemical kinetics*" .[23] Starting from this first research, Enzo Ferroni began a long academic career that allowed him to open many new research fields in physical chemistry that the time will reveal being characterised by the strong impact on the history of chemistry.

This paper aims to reconstruct the milestones of the academic life of this scientist, individuating the five topics which demonstrate the remarkable visionary capacity of this man to open new horizons in his field of research, creating research paths that nowadays appear normal and foregone but that at the time of Ferroni's work were completely uncharted and for which it was impossible to foresee the success they would have. By initially looking at his pioneering studies on colloids, surfaces, and interfaces, the present study is devoted to following how Ferroni sensed the importance of the nascent resonance spectroscopies and surface diffraction techniques, the fruitful relationship between chemistry and cultural heritage conservation, the new frontiers in soft matter, and the strategic role played by applied chemistry, technology, and industry. Finally, the study aims to show that some of the most current topics in chemistry, such as supramolecular chemistry, self-assembly, nanoscopic world, nanomaterial chemistry, scientific diagnostics in cultural heritage conservation, and soft matter, were already outlined in the studies and research Enzo Ferroni designed and carried out.

2. THE BEGINNING: COLLOIDS, SURFACES, AND INTERFACES

Ferroni started his research activity at the beginning of the second half of the 20th century: indeed, his first two articles[23, 24] clearly showed the direction he wanted to pursue, i.e., physical chemistry of colloids, surfaces, and interfaces. One of these systems' most peculiar physical properties is surface tension, which became the first topic on which Ferroni focused his attention and desire to deepen his knowledge. Ferroni intuitively knew that the works by three Nobel laureates in the chemistry of the last decades, namely, Richard A. Zsigmondy (1925), Theodor Svedberg (1926), and Irving Langmuir (1932)[2] could be fundamental milestones and the basis for a new branch of physical chemistry in Italy. In particular, he read with great curiosity and interest Langmuir's papers,[25-53] from which the crucial and peculiar role of the solid-liquid, solid-gas, solid-vacuum, and liquid-gas interfaces emerged, indicating that surface chemistry was fundamental in determining the physicochemical mechanisms of a vast multitude of phenomena.

At the beginning of his research career, Ferroni was attracted by the liquid-gas interface. His attention was focused on measuring the surface tension of many liquid systems in static or dynamic conditions.[54-58] These first studies were also the result of the interaction with the group of Raymond Defay (Anderlecht, 1897 – Brussels, 1987)[59] and Ilya Prigogine (Moscow, 1917 – Brussels, 2003)[60] at the Université Libre de Bruxelles with whom Ferroni had collaborations, even spending time at their laboratories in Brussels. Indeed, during these years, Ferroni's scientific activity converged with the studies of these two great scientists, as proved by the subject of some of their publications[61-66] focused on surface tensions of many different liquid systems. Moreover, the proof of these relationships is given by correspondence dated some years later, also denoting a friendship, from which we report, in Figures 1 and 2, two letters (from Raymond Defay to Ferroni and from Ferroni to Maria Prokopowicz Prigogine, the second wife of Ilya Prigogine) coming from Ferroni's Archive.[67,68] The research on the liquid-gas (air) interface was immediately extended to the bulk of the liquid that contained surfactants to investigate critical micellar concentration,[69,70]


Université Libre de Bruxelles

Bruxelles 5, le 8 novembre 1965.

ECOLE POLYTECHNIQUE
FACULTE DES SCIENCES APPLIQUEES
50, Avenue F.-D. Roosevelt

CHIMIE PHYSIQUE
Service du Professeur Raymond Defay
TELEPHONE : 49.00.30
(secrétariat : ext. 3024)
A rappeler dans la réponse

Monsieur le Professeur Enzo FERRONI,

UNIVERSITA DE CAGLIARI,
INSTITUTO CHIMICO POLICATTEDRA,
72, Via Ospedale.

Mon cher Collègue,

J'ai bien reçu votre lettre du 25 octobre et je suis certes très intéressé par les expériences sur les changements de phases dans les films d'adsorption.

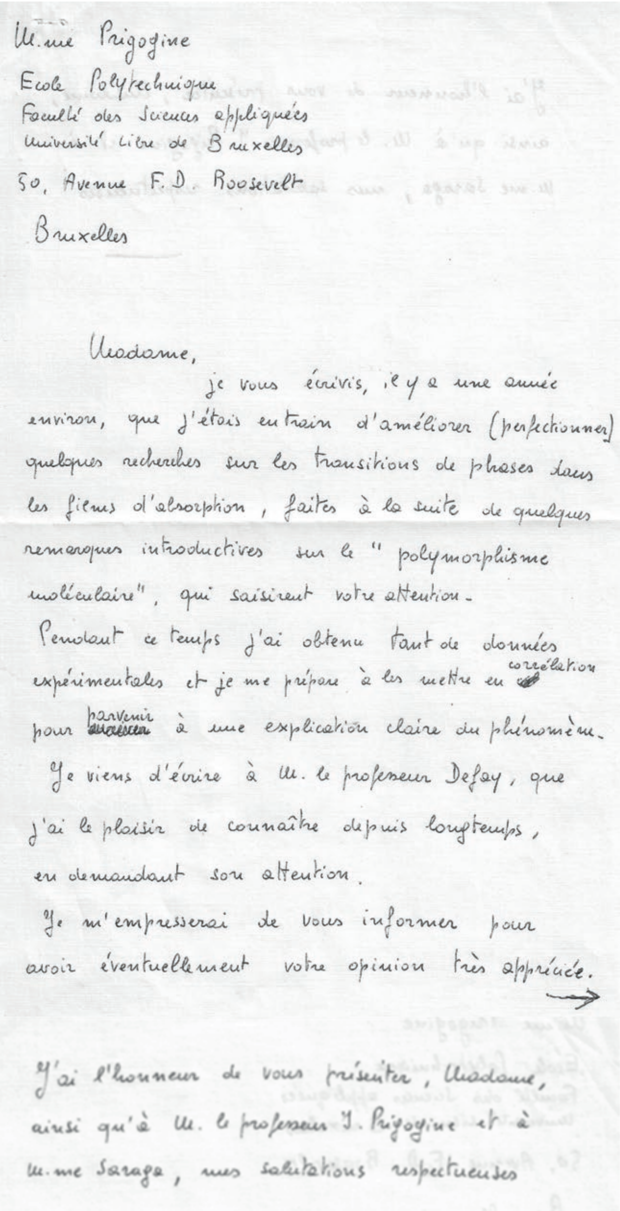
Je n'ai, malheureusement, aucune habitude des problèmes qui concernent les solutions de hauts polymères. Je ne sais donc pas si je pourrai vous aider à éclaircir ceux-ci mais je veux bien essayer d'y réfléchir un peu, si vous me dités de quoi il s'agit.

Je serai fort occupé jusqu'à la fin du mois de janvier. Après cette date, j'èspère disposer de plus de temps pour une réflexion sérieuse.

Recevez, mon cher Collègue, l'expression de mes meilleurs sentiments.

Raymond Defay

Figure 1. Letter by Raymond Defay, Université Libre de Bruxelles, to Enzo Ferroni dated 8 November 1965. "*My dear Colleague, I received your letter dated 25 October, and I am surely interested in your experiments on phase transitions in adsorption films. Unfortunately, I have no experience dealing with high molecular weight polymers in solution. Therefore, I am not certain I will be able to elucidate your doubts, but I am happy to try and ponder on it if you state exactly the precise question. I will be quite occupied with many commitments until the end of January. After this date, I hope to have enough time for a deep and serious reflection. Please accept, my dear Colleague, my best regards, yours sincerely, Raymond Defay*". (Translation by the author).



M.me Prigogine
Ecole Polytechnique
Faculté des Sciences appliquées
Université Libre de Bruxelles
50, Avenue F.D. Roosevelt
Bruxelles

Madame,

je vous écrivis, il y a une année environ, que j'étais en train d'améliorer (perfectionner) quelques recherches sur les transitions de phases dans les films d'absorption, faites à la suite de quelques remarques introductives sur le "polymorphisme moléculaire", qui saisirent votre attention.

Pendant ce temps j'ai obtenu tant de données expérimentales et je me prépare à les mettre en corrélation pour parvenir à une explication claire du phénomène.

Je viens d'écrire à M. le professeur Defay, que j'ai le plaisir de connaître depuis longtemps, en demandant son attention.

Je m'empresserai de vous informer pour avoir éventuellement votre opinion très appréciée.

→

J'ai l'honneur de vous présenter, Madame, ainsi qu'à M. le professeur I. Prigogine et à M.me Saraga, mes salutations respectueuses

Figure 2. Draft of a letter by Enzo Ferroni to Maria Prokopowicz Prigogine, the second wife of Ilya Prigogine. "*Dear Madame, I wrote you just one year ago that I was improving (fine-tuning) some research on phase transitions in adsorption films, carried out following some remarks about the "molecular polymorphism" that grabbed your attention. During this time, I have obtained several experimental results and I am going to put them in a good correlation frame to draw some concluding considerations able to explain this phenomenon clearly. I have just written to Professor Defay, whom I have known for a long time, asking for his comments and suggestions. I shall inform you without delay to ask for your much appreciated opinion if you would. Please accept, Madame, and extend my best regards to your husband, Professor I. Prigogine and M.me Saraga. Yours sincerely, Enzo Ferroni*". (Translation by the author).

polymerisation,[71,72] electrophoresis,[73] aggregation phenomena,[74,75] and equilibrium constants and complex formation.[76,77] Following the path traced by Langmuir, Ferroni continued his pioneering work for building a school of colloids, interfaces, and surfaces in Italy, extending his studies to monomolecular films at the liquid-gas interfaces but also starting to explore solid-gas and solid-solid interfaces. His attention was concentrated on polymorphisms at the interface,[78-81] mono- and multilayers of organic substances,[82,83] adsorption onto solid surfaces,[84] solid → gas reactions,[85] and epitaxy.[86,87]

Ferroni's intense work resulted in a remarkable scientific impact in the physical chemistry of condensed phases following the research lines of two great schools, that of Irving Langmuir at General Electric Company Laboratories, Schenectady, USA, and of Raymond Defay and Ilya Prigogine at the Université Libre de Bruxelles, and allowed him to gain the chair – full professor in physical chemistry – at the University of Cagliari in 1961 presenting 85 scientific publications,[88] including three articles on the *Journal of Physical Chemistry*,[76] the *Journal of the American Chemical Society*,[84] and *Nature*.[79] In 1965, he succeeded in gaining the same chair at the University of Florence, Faculty of Mathematical, Physical, and Natural Sciences, where he remained until his retirement in 1996, becoming Emeritus the subsequent year. During the years spent at the University of Florence, he was Director of the Institute of Physical Chemistry (1965 – 1968), Dean of the Faculty of Mathematical, Physical, and Natural Sciences (1968 – 1971), Rector (1976 – 1979), and Head of the Chemistry Department (1983 – 1985).[89] From 1961 until the end of 1965, when he returned to the University of Florence, he continued his activity in Cagliari[90-99] cultivating his pupils Enzo Tiezzi (Siena, 1938 – 2010) and Gianfranco Rovida (Rome, 1939), who followed him at the University of Cagliari after getting their chemistry master's degree at the University of Florence in 1963 under the supervision of the young colleague Giulio G. G. T. Guarini (Forlì, 1932 – Florence, 2015). Another pupil of Ferroni's, older than Rovida and Tiezzi, was Gabriella Gabrielli (Cortona, 1930 – Florence, 2022), who had already published many papers with Ferroni.[55-57, 74-76, 79-81] To the same team, even though not his pupils, belonged Silvano Bordi, almost a peer of Ferroni's (Florence, 1922 – 1995) and Rolando Guidelli (Florence, 1938) who, taking inspiration from the school of large interface systems founded by Ferroni, would go on to develop the physical chemistry of surfaces and interfaces in electrochemistry.[89]

The path was then traced during the two decades 1950-1970, and the consecration and consolidation of the Italian school on colloids, interfaces, and surfaces founded by Ferroni came in 1993 (*vide infra*) with the foundation of the Italian Centre for Colloids and Surfaces (*Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase*, CSGI) which is still active. Enzo Ferroni was its President from the foundation until his death in 2007; its director for over 25 years was Piero Baglioni (Florence, 1952), who graduated in chemistry under the supervision of Ferroni in 1977, with the dissertation "Membranes selectively permeable to gases". Baglioni succeeded in continuing the legacy and of his Maestro, leading the CSGI to become a Centre of Excellence highly regarded all over the world.[99]

Figure 3. Photo taken during a coffee break at the International IUPAC Congress of Chemistry, Moscow, 12-18 July 1965: from left to right Enzo Ferroni, Enzo Tiezzi, and Boris Vladimorovič Derjagin.

3. THE ADVENT OF RESONANCE SPECTROSCOPIES AND SURFACE DIFFRACTION TECHNIQUES

When Ferroni returned to his hometown, he found a group of young scientists, partly pupils of his, partly of other colleagues at the University of Florence: the first group included the already mentioned Gabrielli, Guarini, Rovida, and Tiezzi; in the second one he found Bordi and Guidelli; and finally in the third Giorgio Taddei (Florence, 1935 – 2019), Mario Pio Marzocchi (Arezzo, 1935). A few years later, Giacomo Martini (Pistoia, 1943 – Quarrata, 2012), another chemist, albeit not one of his pupils, joined Ferroni's team. As soon as he got back to the University of Florence on 15 December 1965, Ferroni took over the direction of the Institute of Physical Chemistry[88, 89] and, strengthened by his experience at the University of Cagliari where he held the first chair in Italy of physical chemistry of colloids and interfaces in the academic year 1963-1964,[88] put together a group of scientists devoted to the physical chemistry of colloids, surfaces, and interfaces.

He had already constituted the first seed during 1950-1961, writing some papers with Gabrielli and directing his pupil Guarini to investigate solid interfaces. Still, on his return to Florence at the end of 1965, he had his second great visionary idea, partly generated by a fortuitous case (*vide infra*), sowing the seed for a novel approach to the physical chemistry of large interface systems by exploiting the unique potentialities of the nascent resonance spectroscopies and surface diffraction instrumental techniques. Indeed, Ferroni had already perceived the importance of the spectroscopic approach when he published two papers with Marzocchi[100, 101] studying halogen-amine interactions by infrared spectroscopy, but he had not yet in mind, immediately after the graduation of Tiezzi and Rovida, what topics could represent some new research lines in the field of colloids and surfaces. The fortuitous case originated the research line dealing with Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic and Spin Resonance (EPR/ESR) spectroscopies, while the second idea was associated with the subject of surface diffraction techniques. Tiezzi and Rovida, after graduating in chemistry in 1963, became Ferroni's assistants at the University of Cagliari where they remained until 1965 – Tiezzi – and 1966 – Rovida –, and participated with him in the 20th International IUPAC Congress in Chemistry held in Moscow on 12 – 18 July 1965. Figure 3 shows Ferroni and Tiezzi at the Congress discussing with the Russian chemist and physicist Boris Vladimorovič Derjagin (1902 – 1994), one of the world's most prominent scientists in the field of colloids and surfaces.

But Ferroni was also always eager to hire promising young researchers besides his pupils and consequently, when back to Florence, selected Leo Burlamacchi (Viareggio, 1933), a 1960 graduate from the University of Pisa, to work as a pioneer in the field of EPR/ESR. Indeed, Burlamacchi, as a graduate worked some years in the industry, and in 1965 he attended the laboratories at the National Council of Research, Institute on Microwaves in Florence, founded and directed by the distinguished physicist Nello Carrara (Florence, 1900 – 1993).[102] In these laboratories, two instruments were built for EPR/ESR and NMR measurements. Still, nobody used them since no chemists – the principal users of such apparatuses for physicochemical characterisation – were present there at that time. Therefore, Burlamacchi had been involved in scientific investigations using these two emerging techniques. Ferroni, consulted by Director Carrara, immediately found a fellowship for Burlamacchi, entrusting him with opening new research frontiers. He suggested creating a couple of young researchers – Burlamacchi and his pupil Tiezzi – to introduce EPR/ESR and NMR techniques to the Florence research group on colloids and surfaces. The first papers[103-107] showed that exploring these new frontiers of physicochemical research was possible. It is worth recalling that Tiezzi taught at the University of Cagliari[102] when Ferroni held the chair of physical chemistry there. Even after Ferroni's transfer to Florence in December 1965, Tiezzi continued his activity at the University of Cagliari. Ferroni himself suggested to Enzo Tiezzi to spend one year in the United States to deepen his knowledge of resonance techniques: indeed, during 1966 and 1967, Tiezzi worked in the laboratories of the University of Washington in St. Louis, Department of Physics under the supervision of Samuel I. Weissman (1912 – 2007) with a Fulbright scholarship, developing the use of electron spin resonance, and then as Post-Doctoral Research Associate, at the Department of Botany and Centre for the Biology of Natural Systems of the same University under the supervision of Barry Commoner (1917 – 2012), further refining his skills in the field of magnetic resonance spectroscopies. In particular, Tiezzi started to explore the possibility of using resonance spectroscopies in biology and medicine.[102,108] Tiezzi would always be deeply grateful to Ferroni, stating several times that he considered Ferroni his mentor since the academic year 1957-1958 when he attended his lectures on Fundamentals of Chemistry 2nd course at the University of Florence.[102] When Tiezzi returned to Florence, he was ready to carry out fundamental research using ESR/EPR and NMR spectroscopies collaborating with Burlamacchi and, from 1967, with the young Martini (see above).[109-114] After the Florence flood, in 1967, Ferroni obtained funds to buy the EPR/ESR instrument from Varian that was placed at the Institute of Physical Chemistry of the University of Florence in the city centre, via Gino Capponi, 7-9. Tiezzi would become a full professor in physical chemistry at the University of Siena in 1979 and one of the most distinguished scientists in the world developing, the first in Italy, the concept of sustainability together with other scientists from across the globe. Burlamacchi became a full professor in 1980 at the same University of Cagliari that twenty years before had welcomed Ferroni.

This research line was pursued for many years with the contribution of other people, among which the already mentioned Baglioni, Maurizio Romanelli (Florence, 1943) and Maria Francesca Ottaviani (Florence, 1951; later Sandra Ristori (Florence, 1960) also joined the team. The research was developed in collaboration with Larry Kevan (1938 – 2002) at the Chemistry Department of the University of Houston. Many papers were published over several years, finally extending their scope to large interface systems, as it was in Ferroni's mind.[115-139] It is worth mentioning that Ferroni appeared only a few times as co-author of these studies of which he was a staunch supporter: we recognise in this behaviour both a commendable generosity and a habit of mind diametrically opposed to what one might imagine in the common sense of the university barony, and intellectual honesty, since Ferroni was aware that he had no skills in resonance techniques when he suggested to Burlamacchi to start his adventure with EPR/ESR and to Tiezzi with NMR. The fortuitous case allowed Ferroni to meet Nello Carrara and Leo Burlamacchi and to create the conditions for the subsequent development of resonance techniques in the Florence colloids and surfaces group headed by Ferroni.

The second route associated with his visionary idea to apply new instrumental techniques to colloids and surfaces studies dealt with surface diffraction techniques. Ferroni set the goal to understand atomic and molecular mechanisms at the basis of gas adsorptions on well-characterised surfaces, namely {hkl} metal monocrystal faces. To realise this objective Ferroni encouraged his pupil Rovida to spend some months in Paris at Trillat's Laboratories (*vide infra*) to ascertain whether the technique of Reflection of High Energy Electron Diffraction (RHEED) under grazing incidence was able to reach the goal or not. Rovida's trials did not produce reliable results. Indeed, Ferroni was fascinated by the concept of understanding atomic and molecular mechanisms at the basis of gas adsorptions onto solid surfaces. When he was back at the University of Florence, Ferroni had the opportunity to read a brochure illustrating that, thanks to the ultra-high-vacuum instrumentation supplied by Varian Associates, it had become possible to build instrumentations able to collect reproducible and well-interpretable Low Energy Electron Diffraction (LEED) patterns. Ferroni was impressed by the brochure's content, which illustrated this innovative technique's impressive power to study all the phenomena at the solid-vacuum interface, especially to deepen the gas adsorption mechanisms onto well-characterised solid surfaces, namely well-defined crystallographic faces. The future Nobel Prize in chemistry (2007) Gerhard Ertl (Stuttgart, 1936) was involved in these studies, and two years later he published a ground-breaking article that opened vast horizons for surface science studies.[140] Ferroni grasped the opportunity and gave Rovida the brochure asking his opinion about the new LEED instrumentation. The answer was positive and a new and fascinating challenge started. Ferroni obtained funds to order the LEED apparatus, which arrived in the autumn of 1966. Still, it had to remain at the customs offices for several months due to the Florence flood (*vide infra*) that had damaged the Institute of Physical Chemistry of the University. Finally, during the spring of 1967, the LEED instrument arrived, was installed, and in a short time, the first two articles on surface studies by LEED from the University of Florence Institute of Physical Chemistry were published.[141, 142] Once again, the path was open thanks to a scientist who constantly desired to see farther, to guide his pupils, but simultaneously leave them free to unleash their talents and abilities without undue pressure or need for complacency and flattery towards him. In the following years, the group that welcomed Ermanno Zanazzi, Marco Torrini, Ugo Bardi and Andrea Atrei gradually came to be headed by Rovida and published many important papers,[143-157] establishing international cooperations, among which the most meaningful was that with Gabor A. Somorjai (1935), University of California, Berkeley.[158, 159]

4. FLORENCE FLOOD (1966): CHEMISTRY AND CULTURAL HERITAGE CONSERVATION

As it is well known[160] the dramatic event of the Florence flood on 4 November 1966, caused a great echo across the world, mainly because of the extensive damages suffered by the exceptional concentration of cultural heritage present in the city. This echo is well condensed in the book *Dark Water* by Robert Clarke: "*There is Florence and there is Firenze. Firenze is the city where the citizens of the capital of Tuscany live and work. Florence is the place where the rest of us come to look*." [160] Ferroni had been back in Florence for just a year and he was immediately involved with all his other colleagues in rescuing damaged instrumentations, books, documents, chemicals, laboratory glassware from the Chemistry Institutes (see Figure 4) in the centre of the city where the Arno's water reached ca. 1 m of height. After the emergency of the first few days, it appeared clear that the damage to the works of art was vast, especially for the wall paintings that could not be removed. Ferroni understood that a scientific approach was essential to help in solving the myriad of problems that conservators and cultural heritage officials encountered. During those frantic days Ferroni was able to invent two different methodologies and simultaneously inaugurate a new epoch for conservation and restoration, the scientific approach and the continued and constant integration between art history, conservation, science and specifically chemistry.[161]

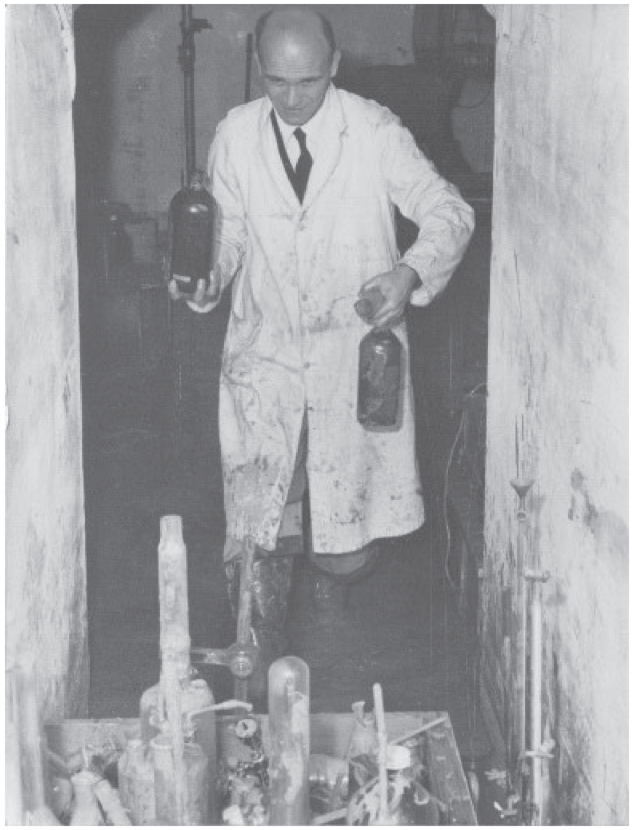


Figure 4. Enzo Ferroni rescuing some laboratory glassware from the cellars of the Chemical Institutes of the University of Florence some days after November 4, 1966.

The first dramatic emergency came from the rapid deterioration of the fresco *L'ultima cena* (*The last supper*) by Taddeo Gaddi (ca. 1300 – 1366) in the Refectory of Santa Croce Basilica. After the waters receded the consequent salt efflorescence due to nitrates was rapidly causing the colour to fall off the wall. This masterpiece was literally vanishing before the anxious eyes of the experts. The only solution was to urgently detach the fresco from the wall and transfer it onto another suitable support. Unfortunately, the detachment was made impossible due to the very high nitrates concentration into the water impregnating the porous structure of the wall. This high ionic force inhibited the sol → gel transition of the animal glue solutions used to impregnate both the paint surface and the canvases onto which, after the gelation of the animal glue, the painting layers would have had adhered allowing the detachment of a few microns of pictorial mortar. The situation was desperate; each day that went by, the coloured powder was found at the feet of the fresco. Ferroni remembered some of his studies[96, 162] where he had demonstrated that tributyl-phosphate

(TBP), an organic compound almost insoluble in water (only 6 g/L at 20 °C)[163] and with very low surface tension (27.79 mN/m at 20 °C),[163] forms monomolecular films onto nitrates water solution with an average molecular area depending on the cations, due to the formation of the different complexes at the water-air interface. He thought that wetting the wall surface with TBP would lead to monomolecular films spread onto the aqueous nitrate solution layers, which adhered to the solid particles of both the mortar and the pigments, besides filling the wall pores. In a way, he prefigured that in this manner, the whole exposed surface of the first layers of the wall would become highly hydrophobic due to TBP, forming a sort of impermeable film that would prevent the migration of the ions coming from the nitrates into the animal glue solution, which therefore would be able to gel and allow the subsequent detachment.[164, 165] The various experts were very sceptical about this hypothesis, and Ferroni replied as Isaac Newton: "*hypotheses non fingo*, please try!" The trial was carried out by the restorer Dino Dini on a small portion of a less famous fresco by Jacopo Ligozzi (ca. 1547 – 1627) and the result was astonishing: the glue set, and the small portion could be easily detached. The whole fresco by Gaddi was then subjected to the same treatment, detached, and repositioned in the same place onto appropriate support. It is still there in good health: it was an actual rescue rather than a restoration or conservation intervention. Without this most significant and brilliant idea by the chemist Ferroni, we would not be able to admire this wonderful work of art now.

The second critical question about wall painting damage was the worsening of the degradation by a process called sulphatisation.[166] The transformation of the binding $CaCO_3$, formed by the setting of lime, into gypsum ($CaSO_4 \cdot 2H_2O$) resulted in a severe deterioration of the painted surface with formation of white patinas, crusts, powdering, and other dangerous pathologies that compromised both the reading and the stability of the pictorial surface: it was evident that the flood had visibly accelerated this phenomenon. Again, Ferroni activated his brilliant and eclectic mind and proposed to re-convert gypsum into $CaCO_3$ by using ammonium carbonate followed by a barium hydroxide treatment. To ascertain whether this chemical approach was effective in recovering a readable and compact painting surface, Ferroni remembered both his time at the CNRS Laboratoire de Diffraction des Rayons X at Bellevue in France and the correspondence[167] with its Director Jean Jacques Trillat (Paris, 1899 – Versailles, 1987). Trillat was a very distinguished scientist with expertise in colloids and interfaces. In 1956 he authored a fundamental book[168] and precursor of the studies that would be developed in Italy by Ferroni, such as those on molecular layers of fatty substances on metals.[169] Reflecting on these memories, Ferroni and co-workers measured the reconversion of gypsum to $CaCO_3$ using ammonium carbonate and subsequent barium hydroxide treatment by X-Rays Diffraction (XRD) using an apparatus invented by Trillat and reconstructed at the Institute of Physical Chemistry of the University of Florence.[170] The results were extremely encouraging since the XRD patterns were in agreement with a total reconversion (see Figure 5). The successive application on the wall painting *San Domenico in adorazione del crocifisso* (*St. Dominic in adoration of the crucifix*) by Beato Angelico (ca. 1395 – 1455) at the San Marco Convent in Florence showed excellent results, not only in terms of reconversion but also in firmly consolidating the painting surface and the thin layers of mortar (*intonaco*) underneath.[171] During the subsequent years and up to the present day, this technique became the legacy of wall painting conservators worldwide. It was named the Ferroni-Dini method after the chemist inventor and the conservator who devised and applied the procedure.[172-178]

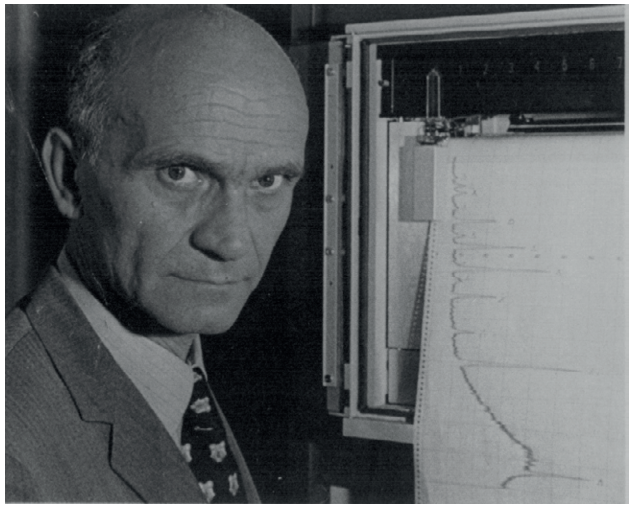


Figure 5. Enzo Ferroni close to a flow chart recorder during the collection of XRD to ascertain the mechanism of the frescoes' sulphatisation and the reconversion to calcium carbonate thanks to the treatment with ammonium carbonate followed by barium hydroxide, the so-called Ferroni-Dini method.

Ferroni's passion for connecting science and art continued throughout his life, and several other studies testified to the outstanding contribution this chemist made to the world of cultural heritage conservation: autogenous lime-based grouts[179-181] and oil-in-water microemulsions[182-185] used for the conservation of wall paintings by Masaccio (1401 – 1428) in the Brancacci

Chapel[164, 165, 186-188] in Florence, the role of the deliquescent salts[189, 190] for the deterioration of the wall paintings of *La leggenda della vera croce* (*The legend of the true cross*) by Piero della Francesca (ca. 1412 – 1492) in the San Francesco Basilica in Arezzo,[191] the chemical stability of some pigments[192] or solvents[193] used for cleaning pictorial surfaces, until his last intuition about a possible role of nanoscience and nanotechnology[194-199] for a revolutionary approach to conservation and restoration. Ferroni had been convinced ever since that the studies dealing with the physical chemistry of colloids and interfaces with potential applications for cultural heritage conservation had to be considered on par with traditional physicochemical papers. Towards the end of his long career, he received a prestigious award when the Journal named after the scientist that was Ferroni's inspiration, Irving Langmuir, decided to dedicate the cover of its 26th issue of 1999, published on 1 December to a photo illustrating the damage done by salt efflorescence in wall paintings. The image was the damaged face of Christ in *The last supper* by Taddeo Gaddi, which Ferroni had rescued about thirty years before. The article[200] was penned, among others, by two of Ferroni's pupils, Piero Baglioni and the author of the present article. Subsequently, many renowned international journals accepted papers on the physical chemistry of colloids and interfaces devoted to bringing a contribution to the improvement of cultural heritage conservation and sometimes dedicating again their covers[201]: Enzo Ferroni's challenge was definitively won at the beginning of the 21st century, as testified by various papers[201-208] that received critical reviews .[209-220]

5. NEW FRONTIERS IN SOFT MATTER

As previously written, at the beginning of the 1990s, the physical chemistry of colloids and interfaces was well cultivated at the Department of Chemistry of the University of Florence into which, in 1983, the Institute of Physical Chemistry was merged. There were at least six sub-groups that germinated from the seeds sown by Ferroni: the teams of monolayers and Langmuir-Blodgett films (Gabrielli with her pupil Gabriella Caminati, Florence, 1960), surface diffraction techniques (Rovida), ESR/EPR (Martini), solid-state reactions and solid-gas interfaces (Guarini), scattering techniques (Baglioni), and electrified interfaces (Guidelli). Moreover, in almost all the Universities in Italy, there were scientists actively working on these topics and the discipline that forty years before was almost inexistent in Italy was in excellent health. During the second part of the 1970s and the entire 1980s, Ferroni pointed his attention to monomolecular films constituted of polymers.[221-231] This interest had been certainly inspired by his previous relationship with the Nobel laureate Giulio Natta[167] and by the Flory-Huggins theory[232-234] for polymer solutions. Indeed, one of the articles Ferroni published in these years directly involved Huggins[221]. The results of a study on the bi-dimensional state conformation of poly β-benzyl-L-aspartate were compared precisely with Huggins' theory.

Ferroni's interest in surface properties of polymers was also stimulated by reading the studies by de Gennes: the future Nobel laureate in physics (1991) considered the physical chemistry of polymers at the interface and their interactions with surfactants as one of the most advanced topics in the physics of the condensed phases.[235-241] The year after winning the Nobel Prize, de Gennes published a short survey on *Science* entitled *Soft Matter*:[242] a new era for physics, chemistry, and physical chemistry was born, and Ferroni would have been pleased to have preconised, some forty years before, that this branch of science had the characteristics to play a fundamental role. In his article,[242] de Gennes explained the peculiarities of this soft matter, often called complex fluids, and he introduced the two main characteristics: complexity and flexibility. He then investigated the various systems that can be considered as belonging to this fourth state of the matter: polymers, surfactants, monolayers, bilayers and multilayers, cell membranes, liquid crystals, micelles, vesicles, and liposomes. This opened a staggering multitude of theoretical and applicative studies in many fields, such as biology and medicine, materials science, technology, and electronics, among others.

Ferroni thought that the times were ripe to launch the institution of a National Centre for Colloids and Interfaces. On 4 May 1993, a new Government was constituted with Prime Minister Carlo Azeglio Ciampi (Livorno, 1920 – Rome, 2016), the future President of the Italian Republic, and the chemist and industrialist Umberto Colombo (Livorno, 1927 – Rome, 2006) was appointed as the Minister for the university and scientific research. Colombo immediately saw the strategic importance of Ferroni's proposal regarding the institution of a National Centre on Colloids and Surfaces, and at the end of 1993, the *Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase*, CSGI – as was called the National Centre for Colloids and Surfaces – was born under the supervision and control of the Italian Ministry for university and scientific research. Ferroni was appointed President, and his pupil Baglioni, Director.

6. APPLIED CHEMISTRY, TECHNOLOGY, AND INDUSTRY

The first mention in the *Chemical Abstract* of Enzo Ferroni as an author is relative to an Italian patent[243] deposited on 27 February 1948 aimed to formulate a thermosetting powder. The young researcher who had carried out a chemistry master's degree thesis on theoretical considerations of chemical kinetics,[22] immediately demonstrated to be interested in aspects dealing with applied chemistry, technology, and industry. Indeed, this feeling and approach would continue throughout his long career and life: Ferroni profoundly understood the deep meaning of IUPAC (*International Union of Pure and Applied Chemistry*), that, as its name implies, focused on the union of pure and applied chemistry.

Among the various aspects of his applied research, we selected four emblematic instances of his approach. First, we thought it significant to recall the ten years of correspondence between Ferroni and Natta from 1958 until 1968, as recently studied by Laura Colli.[167] The interaction between them was intense and found its significant moment just one year after the awarding of the Nobel Prize to Natta: they published a paper in cooperation that linked the two domains of study these scientists had carried out in the last years, that is polymers for Natta and surface adsorbed films for Ferroni.[244]

The second significant contribution was generated by the extended partnership with the Italian entity SnamProgetti operating in the field of fuels and energy. Ferroni was convinced that the idea of SnamProgetti to build a coal pipeline, apparently, a utopian mirage, could actually be pursued since large interface systems as coal-water stable dispersions would be able to generate slurries with suitable fluidity to flow into the pipeline and simultaneously burn at the end of the pipeline without separating the coal from the water. Thanks to some *ad hoc* surfactants Ferroni and co-workers developed stable suspensions of fine powdery coal in water containing up to 70% coal by weight, which was above the threshold required to be burnt without eliminating water.[245, 246] These suspensions are called slurries, and they were heavily investigated[247-249] discovering their viscosity behaviour as non-Newtonian fluids with memory. Ferroni had the idea to involve his friend and colleague, the mathematician Mario Primicerio (Rome, 1932), in the study: the mathematical analysis succeeded in calculating the exact length (security distance) of the pipeline between two contiguous pumping stations to avoid coal sedimentation and stoppage.[250, 251]

Another interesting connection with the industry to find applications of large interface systems has already been mentioned in section 4. dedicated to chemistry applied to cultural heritage conservation. Both autogenous lime-based grouts and oil-in-water microemulsions created during the conservation workshop of the Masaccio, Masolino, and Filippo Lippi wall paintings in the Brancacci Chapel were developed in cooperation with the national industry Syremont S.p.A. whose President at the time was a friend of Ferroni's, Paolo L. Parrini.[179-184]

Figure 6. During the workshop "Energy and industry, financial aspects, technological Innovations: the experience in the textile sector at Prato" held in Prato on 28 November 1980: Enzo Ferroni is the fourth from the left seated at the organisers' table.

Finally, there was the long and fruitful cooperation with yet another industrial sector, Tecnotessile of Prato, founded in 1972 and still actively operating in the field of new technologies applied in the textile industry. Ferroni was designated as President of this Technology Centre right from its inception in 1972. In 1980 he was still collaborating with the textile industry district in Prato (see Figure 6).

The cooperation was mainly dedicated to developing large interface systems able to improve textile production. Ferroni was convinced that soft matter could offer many fruitful opportunities to the textile industry, but at that time, the textile industry was not ready to develop strong synergies with academic research. And again, in this case as well, Ferroni could see ahead of him: at the beginning of the 21st century, some papers from researchers of the CSGI were published, and Ferroni was lucky enough to see them.[252-256] The last of his ideas we will mention is that of UV radiation-absorbing fabrics using nanotechnology; it was again a brilliant idea, but Ferroni was not able to read the paper: it was published online on 30 October 2007, six and half months after the eclectic chemist had passed away.[257]

7. CONCLUSIONS

The scientific activity of Enzo Ferroni, critically revisited and investigated in the present study, allowed us to individuate the main original, novel, and creative ideas developed by this scientist, who operated mainly in the second half of the last century. It showed how he succeeded in creating a new physicochemical school in Italy on colloids, interfaces, and surfaces, a field that the future would reveal particularly worthy of being thoroughly investigated until the end of the 20th century when it became a sort of new state of the matter called "soft", after the studies by the 1991 Nobel laureate in physics Pierre-Gilles de Gennes.

Ferroni perceived this discipline's enormous potential, studying Irving Langmuir's work and deepening his knowledge and skills attending the laboratories led by Raymond Defay and Ilya Prigogine at the Université Libre de Bruxelles. His first visionary idea to develop a branch of physical chemistry, almost neglected in Italy until the end of the Second World War, was followed by his second extraordinary intuition of applying the new and budding resonance spectroscopies (NMR and EPR/ESR) to research, first in solution chemistry and successively to investigate large interface systems.

His eclecticism forcefully emerged in the aftermath of the Florence flood in 1966 when he understood that chemistry, and science and technology in general, could play a fundamental role first in solving the dramatic and urgent problems facing the damaged works of art and then inaugurating a new conception of conservation and restoration, with solid scientific bases and a continuous cross-exchange among different and complementary competencies to create what, in the following years, would become the field of scientific restoration and conservation of cultural heritage. All these merits were acknowledged in the obituary that appeared in *The Independent*.[258]

The consecration of his visionary ideas and intuition arrived in 1991 when Pierre-Gilles de Gennes was awarded the Nobel Prize in physics for having discovered that the methods developed for studying ordinary phenomena in simple systems can be generalised to more complex states of matter, especially liquid crystals, and polymers, individuating soft matter as a peculiar form of matter in the condensed phase. Some new topics, such as supramolecular chemistry, soft matter, self-assembly, nanoscience and nanotechnology, nanoscopic phases, and so on, surely have their root in the colloids and surfaces that Ferroni selected as his main interest for his long academic career.

The paper also showed Ferroni's eclecticism, considering his vision of the relationship between fundamental or basic research and applied chemistry, technology, and connection with industry. Ferroni was always convinced that all aspects of research possessed equal dignity, and the proof of this vision was the close relationship that Ferroni had with the Nobel laureate in chemistry Giulio Natta and the numerous applied studies he carried out having as Partners important companies in the energy, fuels, and textiles sectors.

Thanks to his long and fruitful work, Ferroni received numerous awards, among which we recall: the Gold Medal by the Italian Ministry of the Public Education (1967) as meritorious for school, culture, and art for "his generous collaboration offered for the preservation and recovery of the artistic and cultural heritage of Florence damaged by the flood of 4 November 1966"; the designation of *Grande Ufficiale dell'Ordine* (1977) by the President of the Italian Republic Giovanni Leone (Naples, 1908 – Rome, 2001); the granting of the title *Officier de l'Ordre National du Mérite* (1979) by the President of the French Republic Valéry Giscard d'Estaing (Coblenz, 1926 – Authon, 2020); the title of *Emeritus* in physical chemistry (1997) by the Italian Minister for the university and scientific research Luigi Berlinguer (Sassari, 1932).

The amazing variety of interests and subsequent content of his numerous studies and papers leads to conclude that for Enzo Ferroni, two different statements – the first by Leonardo da Vinci[259] and the second by Primo Levi[260] – can be used to summarise his multifaceted personality. Leonardo stated, "*study science first, and then follow the practice born from that science*" ("*studia prima la scienza, e poi seguita la pratica nata da essa scienza*")[259]. Levi wrote about his the following, speaking about his own chemistry, and we suggest the same is applicable to Ferroni's: "[a] *solitary chemistry, unarmed and on foot, at the measure of man, which with few exceptions has been mine: but it has also been the chemistry of the founders, who did not work in teams, but alone, surrounded by the indifference of their time, generally without profit, and who confronted matter without aids, with their brains and hands, reason and imagination*" ("*chimica solitaria, inerme e appiedata, a misura d'uomo, che con poche eccezioni è stata la mia: ma è stata anche la chimica dei fondatori, che non lavoravano in équipe ma soli, in mezzo all'indifferenza del loro tempo, per lo più senza guadagno, e affrontavano la materia senza aiuti, col cervello e con le mani, con la ragione e la fantasia*").[260] Ken Shulman, in his wonderful book on the Brancacci Chapel,[164] succeeded in masterfully condensing these two quotations in an exceptional sentence: "*Ferroni preferred to work alone, ruminating in his office in the early morning, applying his genially elastic mind until arriving at a solution*".[261]

8. ACKNOWLEDGEMENTS

The author expresses his gratitude to Drs Annantonia Martorano, Andrea De Santis, and Fabio Silari of the University of Florence, Dr Eleonora Todde of the University of Cagliari for the kind collaboration in finding the documents in the various Archives; thanks are also due to Sonia Carla Torretta for the accurate and careful revision of the English language and to Lucia Cappelli, Librarian at *The British Institute of Florence* for the kind assistance. The author also wishes to express his deep gratitude to Gabriella Caminati, Maurizio Romanelli, Marco Fontani, Maria Francesca Ottaviani, and Giulietta Smulevich for the valuable discussions about stories associated with the life of Enzo Ferroni. Section *3. The advent of resonance spectroscopies and surface diffraction techniques* benefited from the invaluable testimonies of Leo Burlamacchi and Gianfranco Rovida, to whom the author expresses his deep gratitude. The financial support of the *Fondi d'Ateneo per la ricerca* from the Department of Chemistry "Ugo Schiff" of the University of Florence is gratefully acknowledged.

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